JOURNAL OF THE AMERICAN CERAMIC SOCIETY

A · MONTHLY · JOURNAL · DEVOTED · TO · THE · ARTS · AND · SCIENCES
RELATED · TO · THE · SILICATE · INDUSTRIES

ABSTRACTS
VOL. 13 NO. 6

VOLUME 17 JUNE - 1934 NUMBER 6

Table of Contents

VOL. 17 JUNE, 1934 No. 6

The Journal of the American Ceramic Society

Glass: the Bond in Ceramics 145
By George W. Morey

Reactions between Solids in the Absence of Liquid Phase 155
By Nelson W. Taylor

Electrolytic Reactions in Vitreous Enamels, Their Relation to the Adherence to Steel 163
By Homer F. Staley

Further Progress Report on the Study of Gases in Enameling Iron 167
By A. N. Lucian and Karl M. Kautz

The Thermal Conductivity of Refractories 173
By Gordon W. Wilkes

Vitrifiable Colors for Decorating Glassware 178
By W. E. Dougherty

Blistering and Crawling of Glazes Caused by Underslip 182
By H. G. Schurecht

Ceramic Abstracts 137

Publication Office: 20th & Northampton Sts., Easton, Pa.
Editorial and Advertising Offices: 2525 N. High St., Columbus, Ohio.
Executive Office: 2525 N. High St., Columbus, Ohio.
Committee on Publications: L. NAVIAS, *Chairman;* L. J. TROSTEL, M. F. BEECHER, R. M. KING, ROSS C. PURDY.
Entered as second-class matter at the post office at Easton, Pa., under the Act of March 3, 1879.
(Copyright 1934, American Ceramic Society)
Subscription twelve dollars a year. Single numbers one dollar
(Foreign and Canadian postage, 50c additional on subscriptions)

Win With Wisdom

- We must join together.
  Federation is essential to betterment in all human affairs.
  Recluses, without communication with other minds, make no advancement and no contribution.
- Each one who federates for mutual benefit must pay his proportionate share of the costs.
  Those who share in the benefits and not in the costs of a federation are not wise, for the benefits to be derived are proportionate to the means made available to the federation.
- THE AMERICAN CERAMIC SOCIETY is a federation to promote ceramic art, science, and technology.
- It pays each corporation to support this federation as Corporation Members at $25.00 per year.
- Individuals engaged in ceramics profit greatly by personal membership at $10.00 per year.
  Present members will profit even further from increases in the number of memberships secured.
- This profit is increased wisdom—without which neither corporations nor persons can win.

The American Ceramic Society

2525 North High St. Columbus, Ohio

GLASS: THE BOND IN CERAMICS*

By George W. Morey

ABSTRACT

A ceramic industry is one which manufactures products by the application of heat to raw materials containing silica or silicates as essential ingredients, and ceramic chemistry is that branch of chemistry which deals with the chemistry of silica. The property which makes silica the basis of industries as apparently diverse as water glass and refractories and which is conferred on all mixtures in which it is present in adequate amounts is that of forming glasses. While silica itself forms an ideal glass, its high melting point requires the addition of a flux, and the commonest and most powerful flux is soda. The addition of soda to silica produces a remarkable lowering of the melting point, from 1713 to 793°, and glass of this composition is remarkably stable against devitrification. It is dissolved by water and forms the basis for the soluble silicate industry. But insolubility in water and acids is essential for most of the glasses of ceramics, and other oxides must be added to obtain this stability. The commonest and cheapest is lime (CaO), and most of the glass of commerce may be regarded as derived from the sodium-silicate glass by the addition of several per cent of lime, usually also with the addition of small amounts of other oxides, notably magnesia, boric oxide, and alumina. Boric oxide and alumina are specially characteristic of the glassy base of enamels, which chiefly differ from glasses in containing insoluble materials to render them opaque and often coloring agents soluble in the glassy phase. Glazes, too, are of similar composition. Refractories are bonded by glass; either a lime glass in the silica refractories, or an aluminum glass in the clay refractories. But a siliceous glass is the characteristic feature which is found in all products of the ceramic art, and glass is the bond which unites the divers ceramic industries.

I. Introduction

(1) Definition of Ceramics Some years ago, a committee of the American Ceramic Society, after a careful etymological study, and due consideration of current usage, defined† the terms "ceramic industry" and "ceramic chemistry." A ceramic industry is one which manufactures products by the application of heat to raw materials which contain silica or silicates as essential ingredients. Ceramic chemistry is that branch of chemistry which deals with the chemistry of silicon and especially of its oxide, silica.

(2) Scope of Ceramics Thus we see that a wide variety of important industries, ranging from the manufacture of water glass to that of refractories, is based on the properties of the one compound, silica. To what property or combination of properties does silica owe its unique position as the basis for so many diversified industries? Consideration of the essential features of each of the ceramic industries will show that the factor common to all is the formation of glass, and that the characteristic property of forming glasses is the property of silica which makes possible the ceramic industry.

Glass is the bond which unites the ceramic industries into a unified group.

(3) Silicate Glass While the ability to form a glass is not an exclusive characteristic of silica and the silicates, when the important properties of permanence in that glassy state and of resistance to corrosion are considered, they stand alone. Borates and, less readily, phosphates, also form glasses, as do various other compounds to a smaller extent, but none of these forms permanent, unalterable glasses as do the silicates. Silica itself gives an almost ideal glass, but its refractoriness makes it unsuitable for manufacture on a large scale, and the glasses characteristic of ceramic products result from the action of fluxes on silica.

II. The Glass Bonds

(1) Sodium Silicate The commonest and most powerful flux is sodium oxide, present as a necessary and added ingredient in many ceramic products and as an inevitable and deleterious impurity in others. As an introduction to ceramic chemistry the binary system, sodium oxide–silica, will be considered. The phase-equilibrium relationships in this system have been worked out in detail,[1] and will be discussed briefly, with special emphasis on their bearing on ceramic products.

These relationships are summarized in Fig. 1, which shows the curves along which the forms of crystalline silica and the two compounds, sodium

* An address delivered at a joint meeting of the Cincinnati Section of the American Chemical Society and the American Ceramic Society, Cincinnati, Ohio, February 15, 1934.

† E. W. Washburn, H. Ries, and A. L. Day, *Jour. Amer. Ceram. Soc.*, **3** [7], 526 (1920).

[1] (*a*) G. W. Morey and N. L. Bowen, *Jour. Phys. Chem.*, **28**, 1167 (1924).
(*b*) F. C. Kracek, *ibid.*, **34**, 1583 (1930).

disilicate and sodium metasilicate, are crystalline phases. Sodium metasilicate melts to a thin liquid at 1089°. On addition of silica, the melting point is lowered until sodium disilicate appears at the sodium metasilicate-sodium disilicate eutectic. On further addition of silica the melting point rises to a maximum at 874°, then falls to the eutectic between sodium disilicate and high quartz. This low-melting eutectic is

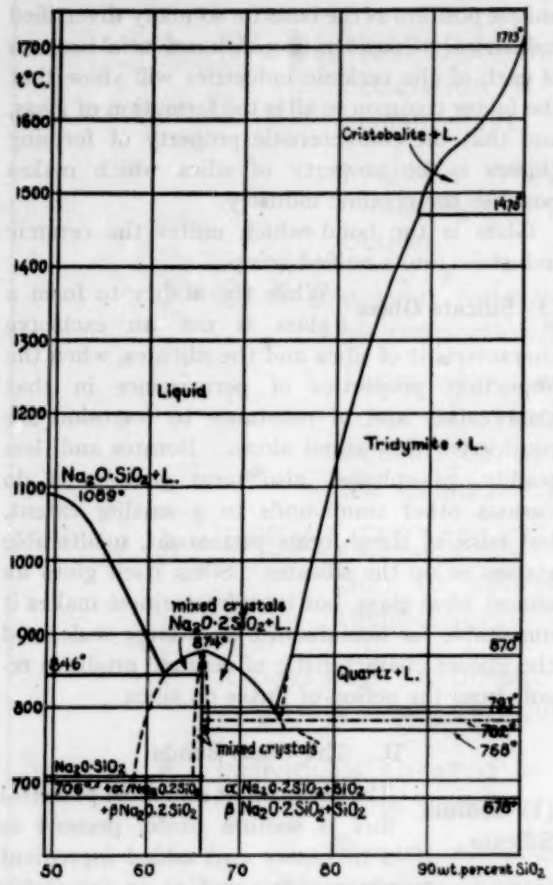

FIG. 1.—Phase-equilibrium diagram of the binary system, Na_2O-SiO_2–SiO_2.

of great importance both in petrology and in ceramics. It represents a lowering of the melting point of silica of from 1710 to 793°, almost 1000°, for the addition of 26% of Na_2O. The lowering of the melting point of silica by alkali oxide is without a parallel, and it is this great lowering which makes possible the glass industry as we know it. At the low temperature of this eutectic the viscosity of the melt has increased to such an extent that it is almost impossible to get the glass to crystallize, even by long-continued treatment at the most favorable temperature.

(2) Methods of Studying Equilibrium Relations in Silicates

The relations shown by this diagram are equilibrium relations, and in the study by which they were determined every care was taken to ensure that equilibrium was reached. The methods of studying phase-equilibrium relationships in silicate systems are different from those commonly used, because of the tendency of silicates to undercool with the formation of glasses.

With salts and metals, the phase transformations may be followed by means of heating or cooling curves. When such materials are heated at a uniform rate an absorption of heat takes place when melting begins, which is indicated by the temperature of the charge falling behind that of the furnace or even remaining constant.

Because of the slowness of the melting process in silicate mixtures such as devitrified glass, no indication of the beginning of melting can be found on the heating curves, and indeed some crystalline silicates may even be heated for a short time many degrees above the temperature of melting without much formation of liquid. This condition is, of course, unstable, and if held above the requisite temperature the crystals will dissolve, but overheating is not an uncommon occurrence. Similarly, the liquid does not freeze readily on cooling, but undercools greatly, and hence the type of discontinuity which gives so marked an effect in the freezing of a metal can not be observed. If held long enough, however, crystals will separate. Accordingly the "quenching" method is used in studying such mixtures.

(3) Quenching Method

A few milligrams of the material, wrapped in thin platinum or gold foil, are held at a known constant temperature long enough for equilibrium to be reached, which may be a matter of hours, days, or even weeks. Then the charge is cooled in such a manner as to freeze the equilibrium and examined with the petrographic microscope. If it is all glass, the temperature of heat treatment was above the liquidus; if a mixture of glass and crystals, it was below the liquidus. By measuring the properties of the crystals they can be positively identified. With difficult mixtures it is customary to have two charges side by side, one initially glass, the other previously crystallized. The heating must be continued long enough for both charges to attain the same condition.

The quenching method is a most convenient method of studying phase-equilibrium relationships, and is to be preferred to the method of heating and cooling curves wherever it can be applied. The microscopical examination leaves no uncertainty of interpretation of the phenomena taking place, as contrasted with the decided uncertainty in the interpretation of thermal curves. The temperature can be determined as closely as the furnace temperature can be controlled, as opposed to the uncertainty in the location of breaks on a cooling curve.

Figure 2 illustrates some heating curves on silicate mixtures, and it is evident that the location of the melting point from such curves[2] is attended with much uncertainty.

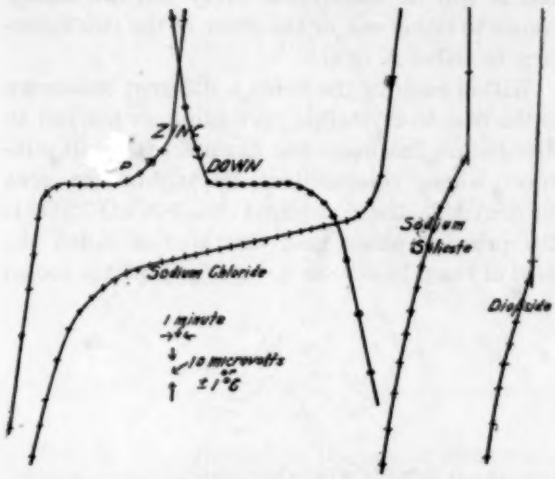

FIG. 2.—Heating curves for zinc, sodium chloride, sodium metasilicate, and diopside, and a cooling curve for zinc.

(4) Silicates Vary in Tendency to Crystallize There is every gradation among silicates in their tendency toward crystallization; and this gradation is dependent not only on the molecular composition of the mixture but also on specific effects of the various added oxides. In general, orthosilicates crystallize so readily that it is not possible to obtain them as glasses, even by the most rapid cooling of tiny melts. Metasilicates crystallize readily but there are great differences between them. Lithium metasilicate can be obtained as glass only by the most rapid cooling of extremely small melts. Sodium metasilicate crystallizes easily, so easily that probably it is not possible to cool a melt of more than 25 grams without its crystallizing, and even then there will be frequent failures.

More siliceous compounds usually crystallize with difficulty. Sodium disilicate is not considered to be especially difficult to crystallize by those experienced in such work, but glass of essentially that composition has long been manufactured on a large scale without this compound ever being observed. But a mixture approaching the disilicate-quartz eutectic in composition can be crystallized only with the greatest difficulty and to obtain it completely crystalline would require a prolonged heat treatment, with frequent fine grinding to render the charge homogeneous. Any ceramic mixture which on crystallizing yields a liquid approaching this eutectic in composition will contain some residual glass, which will serve as a matrix binding the crystalline products together. Glass of approximately this composition is manufactured on an enormous scale, and forms the basis for the large industry of soluble silicates, which is thus a branch of ceramics. Sodium-silicate glass is miscible with water in every proportion; mixtures ranging from dilute water-glass solutions to those containing but a small proportion of water can be prepared, and all but the most dilute are undercooled liquids.

(5) Soda-Lime-Silica Glass The very properties of the sodium-silicate glasses which make possible the soluble-silicate industry cause those glasses to be unsuitable for the ordinary uses to which glass is put. A high degree of resistance to water and atmospheric acids is necessary, and to obtain such a resistance some other oxides must be added to the sodium silicate. Many different oxides will accomplish this purpose, but the one used to the greatest extent by far is lime (calcium oxide), because it is both effective and cheap. Almost all of the glass of commerce is a soda-lime-silica glass, and the ternary system, sodium metasilicate–calcium metasilicate–silica, will next be considered.

The details of this system have been given in several publications,[3] and only the briefest outline will be presented here.

(6) Solid Representation of Isothermal Values The complete representation of the three composition vari-

[2] G. W. Morey, *Jour. Wash. Acad. Sci.*, **13**, 326 (1928).

[3] (*a*) G. W. Morey and N. L. Bowen, *Jour. Soc. Glass Tech.*, **9**, 226 (1925).
(*b*) G. W. Morey, *Jour. Amer. Ceram. Soc.*, **13** [10], 683 (1930).

ables in a plane is made possible by the restriction that their sum must be 100, thus reducing the independent variables to two. Temperature is represented in the third dimension by the vertical distance from the base. The equilateral

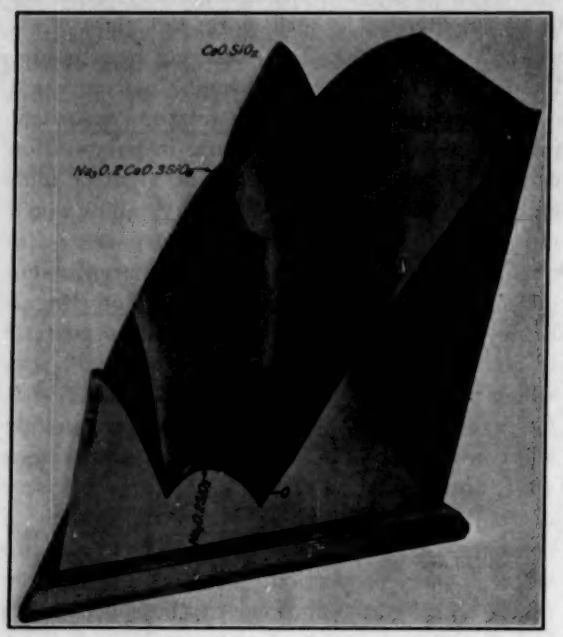

FIG. 3.—Sketch of the solid composition-temperature model, showing phase-equilibrium relations in the ternary system, Na_2O-SiO_2–CaO-SiO_2–SiO_2.

prism (Fig. 3) thus obtained is terminated by a complex upper surface, formed by a number of intersecting sheets, each one of which represents those compositions from which a given compound is the first to crystallize on cooling. The intersection of two such sheets gives rise to a valley, along which two phases separate together from the liquid, and the intersection of three sheets gives a point, an invariant point at which three crystalline phases and liquid coexist, and this coexistence is possible only at the temperature of this point and with a liquid of the composition indicated by the point. In general, when a liquid is cooled under equilibrium conditions, first one of the compounds crystallizes alone, then another one appears and the two crystallize simultaneously, while the composition of the liquid runs down the valley until it reaches one of the two eutectic points. All mixtures high in silica arrive ultimately at the same ternary eutectic, which is closely related to the binary eutectic between sodium disilicate and quartz.

(7) Isothermal Diagrams The crystallization paths can be understood more easily from the usual phase-equilibrium diagrams. If planes be passed through the solid model at successive intervals of temperature and the intersections of these planes with the solid model projected onto the base, the isothermal diagram (Fig. 4) is obtained. This is divided into a number of fields, one for each compound, and the intersections of the fields are represented by heavy curved lines called boundary curves.

Figure 5 shows these boundary curves with the composition of the solid phase in each indicated. If these boundary curves are followed to their end it will be found that every mixture finally comes to either one or the other of the two eutectics, to either *K* or *O*.

Within each of the fields a different substance is the first to crystallize on cooling, or the last to dissolve on heating. For example, from all mixtures whose compositions lie within the area *BCSRNML*, the compound Na_2O-$2CaO$-$3SiO_2$ is the primary phase, and this area is called the field of Na_2O-$2CaO$-$3SiO_2$. As the liquid is cooled

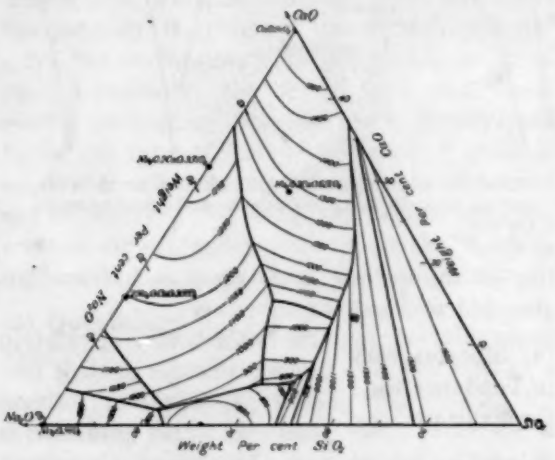

FIG. 4.—Phase-equilibrium diagram of the ternary system, Na_2O-SiO_2–CaO-SiO_2–SiO_2, showing isotherms. (See also *Jour. Amer. Ceram. Soc.*, **16** [10], 513 (1933)).

and more and more of this compound separates, the composition of the residual liquid changes; and since the crystals and the residual liquid are being formed out of the original liquid, all three compositions must lie on a straight line, with the composition of the original liquid between the other two and dividing the line into segments inversely proportional to the relative amounts of

the two phases. As crystallization continues, the composition of the liquid will be continuously displaced on a straight line radiating out from the composition of $Na_2O{\cdot}2CaO{\cdot}3SiO_2$, until that line intersects one of the boundary curves.

If the mixture is in the silica-rich portion of the field, the crystallization path will intersect the boundary curve, *CSRN*, and will end at the ternary eutectic, *O*.

If the original composition is within the field of crystalline silica, the crystallization path will intersect *FOPQTD*, the broken curve which separates the fields of crystalline silica from the

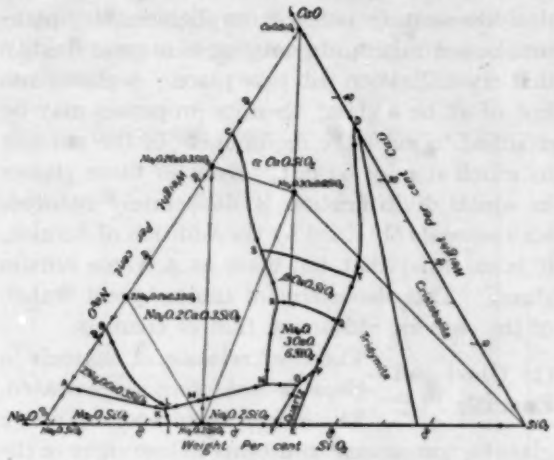

FIG. 5.—Phase-equilibrium diagram of the ternary system, $Na_2O{\cdot}SiO_2$–$CaO{\cdot}SiO_2$–SiO_2, showing the fields of the various compounds, the compositions of the compounds, and the boundary curves.

rest of the diagram. This curve has a minimum temperature at the ternary eutectic, *O*.

If the original composition is within the field of calcium metasilicate, that compound will crystallize first, and the crystallization curve will intersect one of the boundary curves, *CSR*, *RQ*, or *DTQ*. If the intersection is of *CSR*, the metasilicate, $Na_2O{\cdot}2CaO{\cdot}3SiO_2$, will be the second phase to crystallize; if the curve, *DTQ*, tridymite will be the second phase; but in any case when the curve, *RQ*, is reached a reaction will take place.

If the original composition is within the triangle, $Na_2O{\cdot}2SiO_2$–$Na_2O{\cdot}3CaO{\cdot}6SiO_2$–$SiO_2$, the mixture should solidify completely at the eutectic, *O*, to a mixture of these three phases, even though the first phase to crystallize is $Na_2O{\cdot}2CaO{\cdot}3SiO_2$ or $CaO{\cdot}SiO_2$. When the curve *RN* or the curve *RQ* is intersected by a crystallization path, reaction will take place with the resorption of the first formed $Na_2O{\cdot}2CaO{\cdot}3SiO_2$ or $CaO{\cdot}SiO_2$ and the crystallization of $Na_2O{\cdot}3CaO{\cdot}6SiO_2$, a crystalline phase characteristic of devitrified glass, which has been named "devitrite."[4] This compound has such important properties as to warrant some discussion.

(8) Devitrite The field of devitrite is the area *NRQPO*, and the composition is indicated by the point $Na_2O{\cdot}3CaO{\cdot}6SiO_2$. When the pure compound is heated it decomposes into a liquid and crystals of calcium metasilicate, and the mixture does not become completely melted until 1325°. Devitrite is an extreme case of a compound with an incongruent melting point, is strongly dissociated at high temperatures, and is probably present in small proportion even in liquids within its stability field. This may be the reason that it is characterized by an extreme reluctance to crystallize, and all mixtures in which it is a primary phase may be obtained as glass on a manufacturing scale.

Devitrite is formed as primary phase within the area, *ONRQP*, but is a final product of crystallization of every mixture within the area, Na_2O–$2SiO_2$–$Na_2O{\cdot}3CaO{\cdot}6SiO_2$–$SiO_2$, and the crystallization of every mixture within this area leads to the ternary eutectic, *O*. This eutectic is derived from the binary eutectic between quartz and sodium disilicate, the fields of which in the ternary system are separated by the boundary curve, *FO*, along which the temperature falls from 793° at the binary eutectic to 725° at the ternary eutectic. All mixtures near this eutectic are exceedingly difficult to crystallize and are normally obtained only as glass. Any mixture whose crystallization would lead to this eutectic, when crystallized by prolonged heat treatment at the most favorable temperature, will always contain a considerable proportion of glass, unless the heat treatment is exceedingly prolonged and supplemented by repeated fine grinding to secure the homogeneity which has been destroyed by the crystallization process.

The composition region near to and including the field of devitrite contains all the ternary compositions which are possible on a manufacturing scale. The entire region is dominated by the low-temperature eutectic, which makes the region of commercial-glass compositions one of low temperatures in spite of the high silica content

[4] G. W. Morey and N. L. Bowen, *Glass Ind.*, **12**, 133 (1931).

and causes them to be so viscous at their freezing point that crystallization takes place with the greatest difficulty.

The temperatures at which the viscosity of these glasses is suitable for the requisite shaping operations are above the liquidus temperature, so that crystallization is impossible; and at the liquidus temperature the crystals which should separate from the viscous liquid are those of the compound, $Na_2O \cdot 3CaO \cdot 6SiO_2$, which is characterized by an extreme reluctance to crystallize.

If the composition departs from this narrow range, difficulties begin to appear.

If too much SiO_2 is present the liquidus temperature increases rapidly and tridymite separates out with comparative ease.

If too much CaO is present the compound $CaO \cdot SiO_2$ separates easily, because of both the higher temperature and its greater crystallizing ability.

If the glass is in the field of $Na_2O \cdot 2CaO \cdot 3SiO_2$, crystallization takes place still more readily and the glass tends to become too susceptible to decomposition by water.

If the glass is in the field of $Na_2O \cdot 2SiO_2$, there is no danger from devitrification, but the glass is easily attacked by water. It is apparent that the range of composition possible for a soda-lime-silica glass is strictly limited to a small part of Fig. 5, and that the entire diagram is dominated by the low-melting eutectic at *O*.

III. Practical Application to Glassware Making

The problem of the glassmaker is made easier by the fact that he is never dealing with pure soda-lime-silica glasses but rather with glasses containing small but important amounts of Al_2O_3, B_2O_3, and MgO, the effect of each of which is to lower the liquidus temperature and thus to increase the range of feasible glass compositions.

Some of the most noteworthy of the variations from the soda-lime type are the resistance glasses, which are attempts to improve upon the rather inferior resistance to weathering of the original type. These are distinguished first by an increase in the number of components, for chemical resistance is improved by the addition of small quantities of almost any oxide. A second characteristic is the marked increase in the proportions of boric oxide and alumina. Alumina greatly increases the resistivity of a glass, but it also increases its viscosity, thus making it difficult to manufacture. Boric oxide also increases resistivity, but it greatly decreases the viscosity, thus increasing the ease of melting, so the two together make a valuable combination.

In speaking of resistance glasses derived from the soda-silica eutectic, Pyrex brand resistance glass must be excepted for it is unique in being essentially silica, alumina, and boric oxide, with a minimum amount of alkali.

In all the other glasses, however, the dominant feature is the low liquidus temperature resulting from the low-melting eutectic in the system, Na_2O–CaO–SiO_2, and the first requisite for a successful glass composition is that in departing from this low-melting eutectic its liquidus temperature be not raised into a region of so great fluidity that crystallization will take place. A glass must first of all be a glass; then its properties may be modified to meet the requirement of the purpose to which it may be put. Even in those glasses in which divitrification is deliberately induced, such as opals obtained by the addition of fluoride, it is essential that the mass as a whole remain glassy. This also is true of another great branch of the ceramic industries, that of enamels.

(1) Glass and Enamels

The close relation of enamels to glass is not often appreciated. The usual requirement that a glass be transparent causes us to lose sight of the fact that an enamel is essentially a glass, made opaque and often colored by the addition of opacifiers which under the microscope are seen to be disseminated throughout a groundmass of transparent glass.

In composition, the enamels are closely related to the glasses. Indeed, most of them may be regarded as derived from the same low-melting eutectic in the binary system, soda–silica, and closely resemble those glasses to which have been added not only lime but also boric oxide and alumina.

The basic glass of enamels frequently contains greater quantities of alumina than it is customary to use in glasses and usually contains a much greater proportion of boric oxide, added to lower the melting point. Many enamels, like many glasses, contain important quantities of lead oxide, also added to lower the melting point. In general, however, the glassy base of an enamel differs but little from commercial glasses.

To the basic glass are added many different opacifiers: tin oxide, calcium phosphate, calcium

fluoride, which is disseminated as tiny droplets of immiscible liquid which crystallize on cooling, or even clay, which remains as an undissolved residue.

The coloring agent usually is an inorganic oxide soluble in the glass, such as cobalt oxide, although sometimes insoluble colored substances are added.

Enamels also resemble glass in that they are never subjected to prolonged heat treatments in the temperature range within which they are susceptible to devitrification, which is not the case with refractories. The glassy base itself thus rarely shows devitrification, the enamel is essentially a glass, a silicate glass, and hence the enamel industry is a ceramic industry allied to the other members of the group by the presence of the glassy phase.

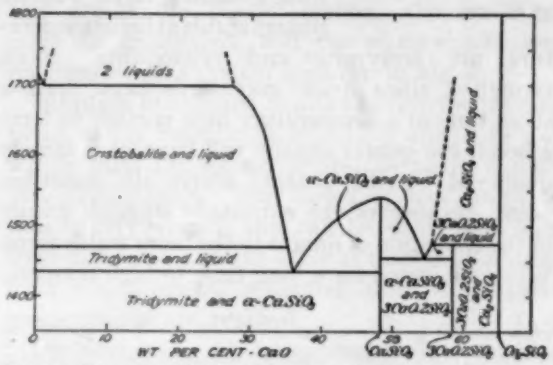

FIG. 6.—Phase-equilibrium diagram of the binary system, CaO–SiO_2.

(2) Glazes Many kinds of ceramic products are covered with a layer of glass, that is, a glaze, which not only renders the porous mass impermeable but also greatly adds to its strength and resistance. Some glazes are first melted into a glass which is then powdered, and the powdered glass is fired onto the refractory.

A "salt glaze" is obtained by reaction of the heated refractory with salt, which produces a layer of glass consisting essentially of alkali silicate, in which are dissolved small quantities of the other constituents of the refractory, especially iron, alumina, and lime. When not properly applied, at too low a temperature, the glaze will be essentially alkali silicate, and be too readily decomposed by water to give satisfactory service under all conditions. When properly applied, however, sufficient quantities of lime, magnesia, and alumina are taken up to make the glaze highly resistant to water and acids. In either case, it will remain a glass, because the mixture formed will be essentially the low-melting eutectic, which is so resistant to crystallization.

The glaze on some of the most refractory types of ware is almost pure alkali feldspar, an excellent glaze because the alkali feldspars are extremely difficult to devitrify and are very viscous even at high temperatures.

Glazes are similar in composition to enamels and glasses, and the composition is suitable for the purpose because of the low-melting sodium disilicate-quartz eutectic, which effectively prevents crystallization and maintains a dense, impenetrable coating of glass over an otherwise porous mass.

(3) Silica Refractories The manufacture of refactories is an important branch of ceramics and one in which the rôle of the glassy phase differs from that in glass and enamels. An important group of refractories is made from silica, usually in the form of quartz, and here the glass is the source of both its strength and its weakness. It is to the glass that the silica refractory owes its initial strength, and the presence of the glass makes possible the structural changes that give it its strength at high temperatures. But at the highest temperatures the glass itself acts as a flux on the brick and leads to its destruction. For the manufacture of silica brick out of quartz, the quartz must be bonded. The usual bond is from 1 to 3% of lime, added during grinding to secure the most intimate mixture.

The effect of the lime can best be seen from Fig. 6, which shows the phase-equilibrium diagram[5] of the binary system, CaO–SiO_2. The crystalline phase at the liquidus is cristobalite. The change from one modification of crystalline silica to another will be discussed later. After a very small addition of lime, which produces a melting-point lowering of only a few degrees, a second liquid layer immiscible with the first is formed. This is an invariant point, and the three phases, crystalline silica in equilibrium with two liquids, can only exist at one temperature. On further addition of lime the temperature remains constant and the amount of the CaO-rich liquid increases, until one layer remains, containing 22% CaO.

[5] This is the most recent revision of the CaO–SiO_2 system, by N. L. Bowen, J. F. Schairer, and E. Posnjak, *Amer. Jour. Sci.* [5], **25**, 273 (1933).

One effect of this formation of two layers is to displace the eutectic composition to a far higher CaO content than would be possible without at the same time greatly lowering the melting point. The composition at the silica-rich eutectic is not greatly different in the two systems, Na_2O–SiO_2 and CaO–SiO_2, but the eutectic temperature in

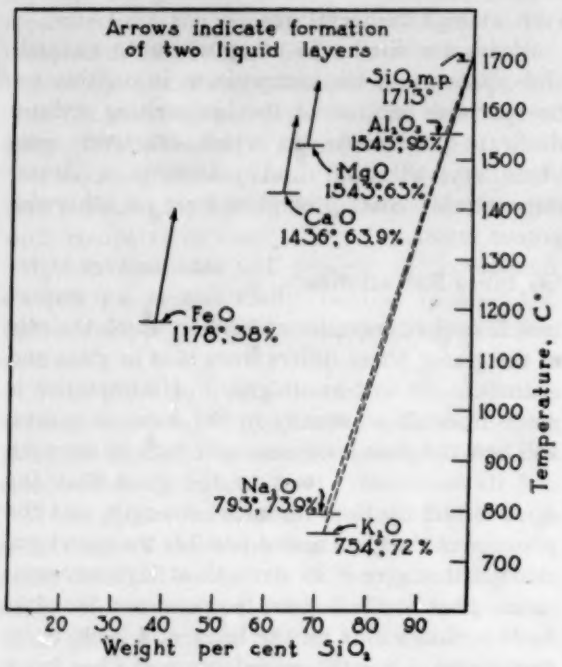

FIG. 7.—Comparative fluxing power of several oxides on SiO_2.

the one case is 793°, in the other, 1425°. Another effect is to cause the melting-point curve to rise very steeply from the eutectic to the temperature of formation of the two liquid layers. Thus the addition of a few per cent of CaO produces a smaller proportion of liquid at the eutectic than would be the case were the eutectic at a lower CaO content, and the mass does not greatly diminish in refractoriness as the eutectic temperature is exceeded. This is because of the very steep rise of the melting-point curve from the eutectic to the point of separation of the silica-rich layer, which is almost at the melting point of the silica itself. This is to be contrasted with the gradual slope of the melting-point curve from the eutectic to silica itself when no immiscibility occurs.

It is interesting to compare the effect of various oxides on the composition and temperature of the silica-rich eutectic; that is, to compare their fluxing power. Figure 7 shows the weight per cent SiO_2 and the eutectic temperature for a number of oxides.

FeO, CaO, and MgO each form a two-liquid-layer system with silica, and the temperature of the eutectics increases in the same order.

The alkali oxides do not show immiscibility, the silica content of the eutectics is about the same as that of CaO and MgO, and the eutectic temperatures are below 800°.

Alumina does not form a two-layer system, and the eutectic is at 5% Al_2O_3 and 1545°.

The presence of alumina or alkali is evidently deleterious to a silica refractory, especially since small amounts suffice to render the two liquids in the CaO–SiO_2 system miscible.

(4) Stable Forms of Silica Silica brick are usually made from ground quartz, but the phases stable at high temperature are tridymite and cristobalite. Even though a silica brick may have been fired a short time at a temperature high enough to form a bond, the quartz usually will have been largely unaltered by the heating above its transition point, because of the extremely sluggish nature of the transition of quartz to the more stable form. When subjected for a long time to high tempera-

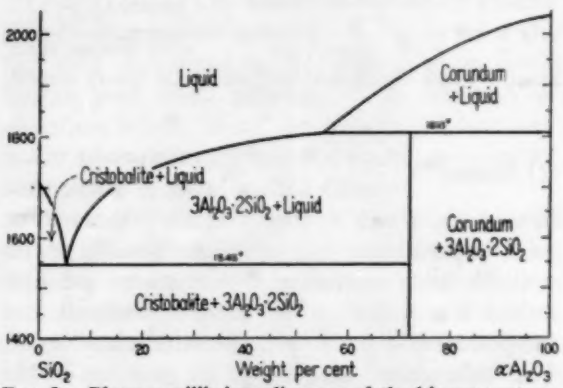

FIG. 8.—Phase-equilibrium diagram of the binary system, Al_2O_3–SiO_2.

ture, however, the quartz will largely change to the stable form under the conditions of temperature prevailing, and the bonding glass serves to accelerate this change into the more stable form.

At the temperature prevailing in a regenerative furnace the brick will usually be largely tridymite, while the higher temperature of a recuperative furnace will give cristobalite. Frequently, however, both forms are found, and it is rare that a brick will be found in which some of the original

quartz has not persisted, in spite of long-time exposure to conditions under which it is unstable. The transition from quartz to tridymite, even in the presence of the flux always present in a silica brick, is a very slow process and the reverse change, from tridymite to quartz, is difficult indeed to accomplish. The glassy bond not only accelerates the inversion but also aids to build up a structure of newly formed crystals such that it maintains the greater part of its strength when the glass becomes a thin liquid.

(5) Alumina-Silica Refractories Another important group of refractories consists of those containing both silica and alumina, ranging from common brick to the kaolin refractories and the more recent mullite refractories. For an understanding of this group the binary system, alumina–silica, must be considered, and the phase-equilibrium diagram[6] of this system is shown in Fig. 8.

Addition of alumina to silica lowers the melting point to the eutectic at 5% Al_2O_3 and 1545°, at which point the second crystalline phase is mullite, $3Al_2O_3 \cdot 2SiO_2$. The liquid of this composition is very viscous and can be devitrified only with difficulty, and the same is true of all liquids from which mullite separates, until the highest temperatures are reached.

On increase in Al_2O_3 content, mullite remains primary phase until 1810°, at which temperature the mullite decomposes with formation of corundum.

Mullite has an incongruent melting point, and when pure mullite is heated it remains unaltered until 1810°, when it decomposes into corundum and liquid, and does not become completely liquid until about 1925°.

When a liquid of the mullite composition is cooled from above the liquidus, it first deposits corundum, and the crystallization of corundum continues until 1810°, when mullite begins to separate. The liquid at this point contains 45% SiO_2, and for equilibrium to be attained it is necessary for this SiO_2-rich liquid to react with the separated corundum to form mullite.

Such a reaction requires time to be completed, and in the ordinary course of events a melt of the mullite composition will form a mixture of corundum, mullite, and siliceous glass but, by proper control, refractories can be obtained consisting essentially of mullite. They are evidently superior refractories. The formation of mullite is characteristic of all refractories made from clay, even from the purest kaolin, and it is found in fire brick as well as in the better grades of porcelain.

Most refractory compositions are made from a mixture of clays, sometimes with the addition of quartz, often with the addition of feldspar. The best clays approach the kaolin minerals in composition and contain about two molecules of silica to one of alumina. When kaolin or a mixture of clays of the same composition is heated, decomposition of the original hydrated minerals first takes place, and the mixture becomes essentially a glass, containing small quantities of fine-grained crystalline material. The amount of crystalline material does not approach that required for equilibrium.

Below the eutectic the mass should consist entirely of mullite and tridymite or cristobalite, but the crystallization of these minerals is slow, and even under the most favorable conditions it is necessary to heat repeatedly with intermediate fine grinding to secure complete crystallization.

If the original mixture contained quartz, it will, as a rule, be found to be slightly attacked, with the most of the quartz remaining as an unaltered core. Even the best of the porcelain type of refractories will be found to be far from the equilibrium condition, and they owe their strength partly to the inert and unaltered quartz and partly to the extreme viscosity of the aluminous glass.

In the discussion of the silica refractories, the contrast was made between the amount of liquid formed at the eutectic for a small amount of lime or alumina added to silica, but there is another important factor which was not considered. The liquid of the composition of the lime-silica eutectic is fluid and it is necessary that the amount of it be small. The strength is due to the structure built up by the recrystallization of quartz to tridymite or cristobalite, and at high temperature this lime-rich liquid is a source of weakness. With refractories containing large amounts of alumina, however, this is not true. While the presence of crystalline material is necessary to give strength, the glassy matrix formed by the firing of a high-grade clay adds to the ability to bear a load because of its great viscosity. Even the addition of feldspar to such a mixture has

[6] N. L. Bowen and J. W. Greig, *Amer. Jour. Sci.* [5], 7, 238 (1924).

not the deleterious effect it might at first sight be expected to have. To be sure, addition of feldspar greatly adds to the amount of glass present, but that glass itself is so viscous that it is not a source of weakness until extremely high temperatures are reached.

(6) Viscosity of Potash Feldspar An experience of mine will illustrate the extreme viscosity of such mixtures. A glass of the composition of potash feldspar, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, good enough to measure the refractive index by the prism method, was wanted. So a mixture of the components in the desired proportions was heated for about a week, with intermediate grinding, at temperatures above 1400°, but the mass instead of melting merely sintered, becoming spongy in texture. Orthoclase has an incongruent melting point, decomposing into leucite and glass at 1150°, so the heat treatment was well above the melting point, and it must have been largely glass. The crucible was then transferred to a gas furnace, where higher temperatures could be reached, and heated as hot as the crucible would warrant. The appearance of the charge did not improve much, so finally the furnace was run a little too hard and melted down the platinum crucible, but the orthoclase glass still was a pumiceous mass, which had made no appreciable progress toward becoming a clear glass and on top of it were globules of platinum. This was at least 600° above the temperature at which melting began and 200° above the temperature of complete fusion.

The presence of a considerable quantity of a glass so viscous as this does not have a deleterious effect until a very high temperature is reached, and it does not impair the usefulness of such refractories in the temperature range for which they are intended.

The effect of the glassy bond on the properties of refractories is highly important and has not received the attention it deserves. Indeed, researches in which the attention is focused on the glass phase and in which drastic changes in the glass composition are made, would be of great value in extending our understanding of the theory of refractories. Kraner,[7] in a suggestive paper on the electrical conductivity of refractories, emphasizes this point. In this connection the effect of heat treatment in producing partial devitrification of the glassy phase, with separation of needle crystals which tend to felt together and thus increase mechanical strength, deserves further study.

(7) Nonrefractory Ware The least refractory ceramic products are made from clays inferior in fire-resisting qualities, usually because of the presence of iron or alkalis, combined with fluxing materials, such as feldspar, calcium carbonate, calcium phosphate, or borax. In most cases such materials are only fired enough to give the requisite strength, but in some cases the amount of glass developed by firing is so great as to produce a translucent material. English "bone porcelain" is an example. In this ware the addition of calcium phosphate enables the manufacture of a light, semitranslucent product of high quality, approaching the best china in appearance but not requiring so high a temperature for firing.

The finest grades of porcelain consist essentially of alumina and silica, in a proportion approximately that of kaolinite, with the minimum of alkali and lime, and so fired that vitrification is almost complete. The major crystalline constituent is mullite, in fine needles, but there is usually some unaltered quartz present, in spite of the drastic thermal treatment. Such ware is almost all glass, but the composition of the glass is such as to give it a much lower coefficient of thermal expansion than ordinary glass, though it does not appreciably differ from Pyrex brand resistance glass in expansion.

(8) Conversion to Mullite Requires Melting For many years it was believed that the alumina-silica compound stable at high temperature was sillimanite, the natural aluminum silicate with the formula $Al_2O_3 \cdot SiO_2$, which was believed to have a congruent melting point. This made it natural to seek for the maximum refractoriness at the 1:1 ratio, but the revision of the phase-equilibrium diagram of the alumina–silica system showed that a refractory of this composition consists of a mixture of mullite crystals and siliceous glass. The most refractory alumina-silica mixtures either approach the mullite composition or exceed it in alumina content. Mixing the ingredients to give the mullite composition, however, is not sufficient to produce a super-refractory. It is necessary that the components be combined,

[7] H. M. Kraner, *Ind. Eng. Chem.*, **23**, 1098 (1931).

and to bring about complete combination is difficult.

One method is the complete fusion of the materials, which crystallize on cooling into a dense, nonporous crystalline mass, practically free from glass. This is possible only by melting in the electric furnace, and an "electro-cast" mullite refractory has recently taken a prominent position in the refractory field.

When made by mixing kaolin with aluminous materials such as bauxite, and firing, as distinguished from melting, it is difficult to obtain even a fair amount of conversion, and the tendency is for such refractories to contain a large proportion of glass, together with fine-grained corundum and mullite. When coarse corundum grains are mixed with kaolin it is almost impossible to do more than coat the corundum grains with glass, so small is the rate of solution. Bowen and Greig, in their fundamental study of the system, found it necessary to heat their mixtures repeatedly with intermediate grinding to fine powder to obtain complete conversion of the glass and corundum to mullite, but that is a process prohibitively costly for the manufacturer. Nevertheless, mullite refractories are now available in which the conversion is sensibly complete, and the product is immeasurably superior to the best refractories of a decade ago. When conversion to mullite is complete, as in an electro-cast refractory, our general rule that the glass is the bond in ceramics apparently is not true, but to attain even these super-refractories entirely free from glass is difficult, and probably some glass will remain in the best of them.

This brief survey has skimmed lightly over the ceramic industries, but even the briefest survey can not fail to bring out the fundamental rôle played by glass in all of them. In each, the property of the formation of glass, characteristic of silica and the silicates, has played the dominating rôle, and the presence of a glassy phase serves as a bond to weld together the ceramic industries.

Geophysical Laboratory
Carnegie Institution of Washington
Washington, D. C.

REACTIONS BETWEEN SOLIDS IN THE ABSENCE OF A LIQUID PHASE*

By Nelson W. Taylor

ABSTRACT

Finely divided solids in intimate contact frequently react chemically with one another. Although the reaction may be greatly accelerated by the presence of a liquid phase, the liquid is not necessary for the reaction. In the presence of a liquid the direction of reaction is usually determined by the formation of an insoluble product or by the production of a gas, but in the absence of a liquid the direction and driving force of the reactions are measured by the free energy change which may be expressed in terms of the lattice or crystal energy of the constituents.

The reactivity of an ionic type of solid is enhanced by those factors which weaken the inter-ionic forces. Such factors are heat, structure rearrangement at transition temperatures, ionic distortion due to polarization, solid solution, etc. Specific-heat curves of solids show temperatures at which they are acquiring considerable vibrational or rotational energy and therefore indicate temperatures at which reactions are possible. High-temperature specific-heat data are greatly needed in connection with the study of reactions of solids.

The lattice type of a crystal of an inorganic substance may be true ionic or it may be essentially an oxide lattice, *e.g.*, $A^{++}BO_4^{=}$ or $AO{\cdot}BO_2$ and the mechanism of reaction will be different. In a reaction like $A'O + ABO_4 = A'BO_4 + AO$, if BO_2 is a volatile oxide, the reaction may consist essentially in a distillation of BO_2 from AO to A'O.

The velocity of a solid-phase reaction is primarily determined by the heat of activation, or "work of loosening" of the constituents. This quantity can be obtained from the kinetic data itself and varies in magnitude from a few hundred calories per mol to rather large values. The greater the value of the heat of activation, the slower is the reaction. Another important factor in controlling the speed is the particle size.

Solid-phase reactions permit the preparation of many materials which can not be made in the wet way. Silica reacts with alkali earth oxides at temperatures as low as 400°C. Lime reacts with sillimanite as low as 530°C to give calcium metasilicate and alumina. In the field of ceramics many structural changes frequently occur far below the eutectic temperature of the system. One example of this is indicated by the marked heat evolution which occurs in kaolin at about 900°C. An important reaction of the Portland cement industry is the dissociation of tricalcium silicate, $3CaO{\cdot}SiO_2 \longrightarrow 2CaO{\cdot}SiO_2 + CaO$, which runs with maximum speed at about 1150°C.

Some practical applications to refractories are mentioned.

* Presented in the Symposium on Crystalline Substances in Refractories, Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February 13, 1934 (Refractories Division). Received February 14, 1934.

I. Introduction

Many ceramic, metallurgical, and geological processes involve chemical reactions between solids in the absence of a liquid phase. In the firing of clays, important structural changes occur in kaolinite at temperatures far below the melting point; in roasting sulfides in the presence of lime and air, sulfates are formed in the dry state; in the operation of the Dwight-Lloyd equipment for sintering of sulfides, recrystallization and chemical changes occur; in the production of special refractories such as MgO, BeO, ThO_2 for electrical insulators, recrystallization and bonding take place; in the heating of iron-bearing chromite and magnesite, reactions such as the formation of ferrites and spinels occur by interaction of the dry constituents; and in many geologic processes which come under the name of thermal metamorphism, minerals like andalusite, spinel, diopside, and garnet appear to be formed as a result of reaction of solids in intimate contact. In the early stages of glassmelting, sodium carbonate and silica react to form the silicate. The well-known reaction between manganese dioxide and potassium chlorate to produce oxygen is probably an example of the same phenomenon, and reactions involved in the dissociation and formation of carbonates may also be mentioned. Phase changes in alloys and development of eutectoid structures are well known to the metallurgist.

Despite the widespread character of such reactions, relatively little scientific attention has been given to the problem in this country. The physical metallurgists have been active in this field and in their knowledge of structure changes in solids they are far ahead of the ceramists. A recent paper by Bowen, Schairer, and Posnjak[1] of the Geophysical Laboratory on the system CaO–FeO–SiO_2 gives a good deal of information on the lime-iron metasilicates, involving wollastonite and hedenbergite solid solutions, but does not give details as to the mechanism of the reactions involved. Nevertheless, the paper does illustrate a method of attack on such problems.

An early paper by Day and Allen[2] on the isomorphism and thermal properties of the feldspars describes the production of albite by sintering the ingredients below the melting point, since attempts to obtain the crystals from a melt were without success. In fact it may be emphasized that the sintering technique will frequently give compounds which can not be obtained from melts, either because of high viscosity or because the compounds in question are unstable at melting temperatures. The method is also superior to precipitation from aqueous solution since hydrates of indefinite composition are commonly obtained in this way.

II. Experimental Methods

For leadership in a scientific study of sintering phenomena we have to turn to Europe. Gustav Tammann of Göttingen has been a pioneer in the field. J. A. Hedvall of Göteborg and W. Jander of Würzburg have also been very active. Goldschmidt has prepared a large number of new compounds, tungstates, molybdates, silicates, titanates, and stannates, by this technique in connection with his studies on the laws of crystal chemistry. W. E. S. Turner of Sheffield has studied the reaction between Na_2CO_3 and SiO_2 in some detail in connection with his work on the fundamental processes underlying glassmelting.

The methods of study have been many. Tammann stirred the finely ground and well-mixed ingredients in a glass tube and gradually raised the temperature. When reaction began and the mixture commenced to recrystallize the stirrer stopped. He was able to show that in many cases the reaction temperature is very nearly that at which one of the ingredients was undergoing recrystallization with grain growth. Furthermore, this temperature was approximately 57% of the absolute melting point in cases where the solid showed no polymorphous inversions. Otherwise, reactions often occurred at a transition temperature.[3]

Tammann also made heating curves, plotting temperature against time, and found certain points where arrests or accelerations occurred in his materials due to endothermal or exothermal effects. Hedvall[4] has made good use of this method and has shown that those factors which weaken the forces in the crystal lattice tend to

[1] N. L. Bowen, J. F. Schairer and E. Posnjak, *Amer. Jour. Sci.*, **26**, 193–284 (1933).

[2] A. L. Day and E. T. Allen, *Carnegie Inst. Publ.*, No. 31. *Cf.* also J. W. Cobb, *Jour. Soc. Chem. Ind.*, **29**, 799 (1910); W. E. S. Turner, *Jour. Amer. Ceram. Soc.*, **17**, [2], 21–25 (1934).

[3] G. Tammann, *Z. anorg. allgem. Chem.*, **126**, 119 (1923); **149**, 21–98 (1925), and many other papers. *Cf.* K. Endell, *Metall u. Erz*, **18**, 1 (1921).

[4] J. A. Hedvall, *Z. angew. Chem.*, **44**, 781 (1931). *Cf.* also *Jour. Phys. Chem.*, **28**, 1316–30 (1924).

bring about reactions. Such factors are heat, lattice distortion due to polarization and to the other materials in solid solution, polymorphous inversions, etc. The use of a differential method, with one thermocouple junction in a neutral body and one in the substance under examination, is more sensitive than the ordinary heating curve, and has brought forth some interesting results. Jander[5] has studied the problem more quantitatively by considering reactions which involve the production of a gas and by making exact rate studies at various temperatures. Several investigators in this country and abroad have used expansion apparatus to measure rates of reaction and of inversion at constant temperature.

The petrographic microscope and the X-ray diffraction camera to identify the reaction products have been used by many investigators, notably among whom is Goldschmidt with his co-workers.[6] Independent studies on electrolytic conduction in ionic crystals have been made by von Hevesy,[7] studies on diffusion in crystal lattices by Smekal,[8] on rotation of ions in the crystal lattice by Pauling,[9] and on specific heat by many investigators. These references are cited to meet the frequent objection that reactions in solids are highly improbable because of the inertness of atoms or ions in solids and their consequent difficulty of diffusion and that, in all probability, some vaporization or sublimation phenomena are involved. One can, of course, never exclude the vapor phase except by application of external pressure, but many reactions occur at such low temperatures as to make the probability of a vapor-phase mechanism almost zero. Thus for example, the reaction $BaCO_3 + SiO_2$ is 5% completed in 2 hours at 774°C. The dissociation pressure of $BaCO_3$ at this temperature is about 0.006 millimeter and that of SiO_2 is negligible. That of BaO is, of course, also negligible. Hedvall states that $BaO + Al_2SiO_5$ react at 357°C with sufficient speed to produce a heat effect. BaO reacts with $CuSO_4$ at 346°C in less than one second, and the products are firmly baked together to give high mechanical strength. Obviously, vapor pressures can play no rôle at these low temperatures.

[5] W. Jander, I, *Z. anorg. allgem. Chem.*, **163**, 1–30 (1927); IX, *ibid.*, **202**, 135–53 (1931); see also *Ceram. Abs.*, **7** [9], 644 (1928).

[6] (*a*) V. M. Goldschmidt, T. Barth, G. Lunde, and W. Zachariasen, "Geochemische Verteilungsgesetze der Elemente, VII," *Skrifter Norske Videnskaps-Akademi Oslo* (1926); Goldschmidt, VIII, *ibid.* (1927).
(*b*) N. W. Taylor, *Z. physik. Chemie*, **B9**, 241–64 (1930).

[7] G. von Hevesy, *Z. Elektrochem.*, **34**, 463–72 (1928).

[8] A. Smekal, *ibid.*, pp. 473–83 (1928).

[9] L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

III. Free Energy Change in the Reaction

When reactions occur between ions in solution the direction of reaction is usually determined by the formation of a precipitate, a gas, or an undissociated molecule. In the case of reactions between two solids we can not ordinarily ascribe the change to such causes. The determining factor appears to be the free-energy change as expressed in terms of the lattice or crystal energies of the solid phases concerned. By definition the lattice energy U per gram-molecular weight of crystalline solid is that energy which is needed to convert it completely to gas ions at infinite dilution, *i.e.*, so far apart that no electrical interaction can occur. Two methods have been used for the evaluation of lattice energies; one is the Born-Haber thermochemical cycle, and the other is a direct calculation from the electrostatic theory of the crystal lattice. Only the former will be given here. Table I gives the numerical values of U for several halides.

TABLE I

LATTICE ENERGIES OF SOLID HALIDES, U

NaF	214 Cal.	KF	189		
NaCl	179	KCl	163	AgCl	207
NaBr	169	KBr	157	AgBr	204
NaI	161	KI	148		

Figure 1 illustrates the thermochemical cycle. MX is taken to be a uni-univalent salt in this particular case.

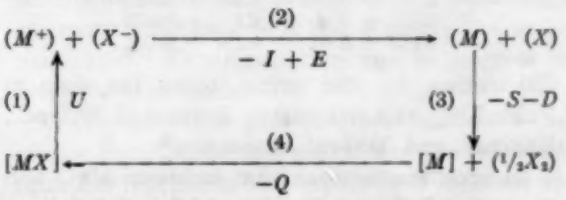

FIG. 1.—The Born-Haber thermochemical cycle for evaluating lattice energies of crystals.

The stages in the cycle are as follows:

(1) The crystal is dispersed into ions.
Energy gain = U (lattice energy).

(2) The ions are converted into monatomic neutral gases.
Energy gain = $-I + E$. I = ionization potential.
E = electron affinity.

(3) The monatomic neutral gases are converted into their standard states at 25°C and 1 atmosphere pressure.
Energy gain = $-S - D$. S = heat of sublimation
D = heat of dissociation.

(4) The elements in their standard states are combined to form the crystal, MX.
Energy gain $= -Q$. Q = heat of formation.

The changes in energy in the system must add to zero; Hence,

$$U - I + E - S - D - Q = 0$$
$$U = I + S + D + Q - E.$$

Let us now consider a reaction between KF and NaCl. From the data of Table I we find

$$179 \text{ Cal.} + [NaCl] = Na^+ + Cl^-$$
$$189 \text{ Cal.} + [KF] = K^+ + F^-$$

$$368 \text{ Cal.} + [NaCl] + [KF] = Na^+ + K^+ + F^- + Cl^- \quad (1)$$

Similarly

$$214 \text{ Cal.} + [NaF] = Na^+ + F^-$$
$$163 \text{ Cal.} + [KCl] = K^+ + Cl^-$$

$$377 \text{ Cal.} + NaF + KCl = Na^+ + K^+ + F^- + Cl^- \quad (2)$$

Subtracting (2) from (1):

$$NaCl + KF = NaF + KCl + 9 \text{ Cal.}$$

This means that solid NaCl and solid KF will react to form solid NaF and solid KCl with the evolution of 9 cal. or 9000 cal. per mol. In view of the fact that $\Delta F = \Delta H - T\Delta S$ and that in these condensed systems, which involve only ion interchange between crystals, the entropy change (ΔS) is practically zero and ΔH may be identified with $-\Delta U$, the quantity 9000 calories per mol may be taken as a measure of the free-energy decrease (ΔF) of the system. The reaction should therefore be spontaneous.[10] Actually it is found to be so.

The products NaF and KCl were identified by Thomas and Wood[11] by an X-ray method. These investigators also found the following reactions to occur:

$$KCl + NaBr = KBr + NaCl$$
$$KCl + NaI = KI + NaCl$$
$$AgCl + KBr = AgBr + KCl.$$

Calculation by the writer, using the data of Table I, shows a free-energy decrease of 2000 cal., 3000 cal., and 3000 cal., respectively.

In such reactions as that between MgO and Fe_2O_3[12] or ZnO and TiO_2[13] or NiO and SiO_2[13] we lack the necessary lattice energy data to make a similar computation. However, an X-ray examination of the sintered mixtures after several hours heating shows $MgFe_2O_4$, $ZnTiO_3$, and Ni_2SiO_4. In every case the reaction temperature was several hundred degrees below the eutectic temperatures of the systems involved, and the materials were of analytical purity.

As lattice-energy data accumulate we may expect to make more extensive and accurate tests of the validity of the principle that the reaction goes in such a direction as to form a system of higher lattice energy or, in other words, a system of lower intrinsic energy content. The best calculation and summary of such data to be found in English at present is by Sherman.[14]

In the case of a dissociation process which goes to the right at higher and to the left at lower temperatures it is obvious that the entropy term in the equation $\Delta S = (\Delta H - \Delta F)/T$ can not be neglected. In general, this will be true of compounds which are formed at low temperatures but dissociate at higher temperatures.[15]

IV. The Rôle of Diffusion in Reactions between Solids

Since reactions between solids in contact involve ionic or atomic interchange between the two crystal phases, it is obvious that diffusion phenomena within the crystals will play an important rôle. That such diffusion may occur is well known. In the first place, the fact that solids have a specific heat shows that the constituent leptons[16] are in motion, and as this heat approaches the upper limit of $3R$ calories per gram-atom, this motion becomes more and more general. At higher temperatures the amplitudes of vibration become still greater until finally the crystal melts. Kordes[17] has shown that in many cases the reaction temperatures coincide with the temperatures of rapid recrystallization. The self-diffusion of lead atoms in a piece of solid lead has been studied with great accuracy by Seith and Keil[18] using an ingenious method, which consisted of measuring the rate of diffusion into the lead of a

[10] For a discussion of free energy and entropy *cf.* G. N. Lewis and M. Randall, Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill, New York, 1923.

[11] E. B. Thomas and I. J. Wood, *Jour. Amer. Chem. Soc.*, **56**, 92–97 (1934).

[12] W. Weyl, *Tonind.-Ztg.*, **53**, 559–62 (1929).

[13] N. W. Taylor, *loc. cit.*

[14] Jack Sherman, "Crystal Energies of Ionic Compounds and Thermochemical Applications," *Chem. Rev.*, **9**, 93–170 (1932).

[15] *Cf.* E. T. Carlson, *U. S. Bur. Stand. Research Paper*, No. 381 (1931) for a more involved case.

[16] According to F. Rinne, the term lepton may be used to include atoms, ions, electrons, and other molecular species. F. Rinne, Crystals and the Fine Structure of Matter. E. P. Dutton Co., New York, 1924.

[17] *Cf.* W. Eitel, Physikalische Chemie der Silikate, pp. 431–37, Leopold Voss, Leipzig, 1929.

[18] W. Seith and A. Keil, *Z. Metallkunde*, **25**, 104–106 (1933).

radioactive isotope of lead (thorium B). They found that the logarithm of the diffusion constant was directly proportional to the reciprocal of the absolute temperature and from this datum derived a value of 27,870 calories per gram atom as the "heat of loosening" or energy of activation of the lead atoms. The diffusion constant at 106°C was 1.45×10^{-11} cm.^{2} per day and at 324°C (4° below the melting point) was 4.78×10^{-6} cm.^{2} per day. It apparently made little difference whether the lead was a single crystal or polycrystalline material. It may be mentioned, however, that lead shows marked tendency to crystal growth at these temperatures. In another paper[19] Seith and Laird studied the diffusion of gold, silver, bismuth, thallium, and tin into lead. At 285°C they found diffusion constants as follows: Au (0.4), Ag (0.79×10^{-2}), Bi (3.8×10^{-5}), Tl (2.7×10^{-5}), and Sn (1.4×10^{-5}). The corresponding "heats of loosening" were 13,900, 15,100, 18,500, 20,900, and 23,900 calories. The authors state that with increasing similarity of the dissolved metal with lead (as measured by the solubility), the diffusion velocity falls off and heat of loosening increases.

Initial stage	A	A	A	A	A	A	B	B	B	B	B	B	B
First step	A	A	A	A	A	B	A	B	B	B	B	B	B
Second step	A	A	A	A	B	A	B	A	B	B	B	B	B
Third step	A	A	A	B	A	B	A	B	A	B	B	B	B
Fourth step	A	A	B	A	B	A	B	A	B	A	B	B	B

FIG. 2.—Interdiffusion of two crystalline phases A and B.

These results are somewhat at variance with the old view that diffusion in solids is facilitated where solid solution occurs. The idea was that if two kinds of atoms were closely related structurally and chemically they could intermingle freely with one another without distortion of the solid lattice. However, we find that the diffusion constant for lead in lead is lowest of all the systems studied and the "work of loosening" is greatest. The present concept would, therefore, be that where the bonds between two kinds of atoms or ions are weak, diffusion may readily take place and the temperature coefficient will be low. As the bond strength increases, the diffusion coefficient falls off and the influence of temperature becomes greater.

If the above-mentioned mechanism is applied to such a reaction as $CaO + SiO_2 \longrightarrow CaSiO_3$, it will be seen that the reaction product $CaSiO_3$ is not an inert barrier but rather an active carrier for further reaction. Two solid phases, A and B, are considered to be in contact, as represented in Fig. 2.

The figure represents the successive stages in the diffusion process and the progressive widening of the diffusion band. The figure is intended to represent a mechanism somewhat as follows: Initially atom B on the phase boundary finds it easier to diffuse into the adjacent phase than into its own because its thermodynamic activity in the adjacent phase is zero and the process of diffusion will involve a large free-energy decrease. The same reasoning applies to atom A on the phase boundary. Accordingly the first step is taken and we now have two phase boundaries instead of one. On the left atom A interchanges with its neighbor B across the boundary, and on the right atom B interchanges with its neighbor A across the other boundary. We now have the second stage. This process repeats until A and B have completely reacted to form AB or at least until one of the components is exhausted. It will be seen that in every case the phase boundaries are the active zones where the reaction process is initiated. It is to be noted, however, that with every advance of the boundaries into phases A and B, interchanges of atomic positions occur within the reaction product, AB. This postulates that in the solid product, AB, the constituent atoms are loosely bound. If they are tightly bound the freedom of this interchange will be diminished. If a high melting product is formed the reaction will tend to be slow unless the temperature is raised accordingly. On the other hand, if the reaction product, AB, shows a transition temperature (where internal rearrangement is occurring), the mutual diffusion of A and B may prove to be very rapid. Experiments are now in progress to test this hypothesis.

With regard to a quantitative expression of the kinetic data, Jander has shown that the following equation represents the results in a satisfactory way.

$$\left(1 - \sqrt[3]{\frac{100 - x}{100}}\right)^2 = \frac{2Dc_0 \cdot z}{r^2} = k'z \qquad (1)$$

and $$k' = Ce^{-q/RT} = C^{-a/T} \qquad (2)$$

where x = per cent conversion.
z = time.
k' = a constant, which depends on the diffusion coefficient, D, and on the particle size, r.
c_0 = concentration of the diffusing particles at the reaction interface.

[19] W. Seith and J. G. Laird, *Z. Metallkunde*, **24**, 193–96 (1932).

q = energy, expressed in calories, which a gram molecule of particles requires in order to be able to move from point to point in the crystal lattice and so permit reaction.

C = a constant, which depends in part on the number of mobile particles, and on the physical state of the material, porosity, etc.

The important quantity q or a is commonly called the "energy of activation" or the "heat of loosening" or the "work of loosening."

It will be seen in the case of uniform spherical particles that a plot of $\left(1 - \sqrt[3]{\frac{100-x}{100}}\right)^2$ against time should give a straight line if the reaction velocity depends on the surface area. Actually such a plot is not quite a straight line but is very nearly so. For a reaction of $BaCO_3$ with Nb_2O_5 (ratio 1:10), Jander obtained the following values for x after 10 minutes at the temperatures, t. Values for k are also given.

t =	624°C.	647°C.	681°C.	691°C.	748°C.
x =	16.7%.	23.8%.	34.0%.	44.1%.	64.0%.
k =	0.00037.	0.00091.	0.00173.	0.00332.	0.00823.

From these data he calculated that

$$k' = 2.5 \times 10^7 \cdot e^{-22,000/T}$$
and q = 43,800 cal. per mol.

For the reaction between $BaCO_3$ and SiO_2 (1:10)

$$k' = 2630 \cdot e^{-20,500/T}$$
and q = 40,800 cal. per mol

It will be noted that the value of C is much larger for the first reaction than for the second, indicating that the first proceeds rapidly at a lower temperature than does the second. On the other hand, the q values do not differ greatly. It will be shown later that in these two cases q is relatively small and that the diffusion process is essentially the factor which limits the speed of the two reactions. This is, however, not always the case, as will be seen later.

In the reaction $CaO + MoO_3 \longrightarrow CaMoO_4$, Jander and Hoffmann found that the "heat of loosening" was independent of the proportions of CaO and MoO_3 in the original mixture, of the particle size, and of the method of preparation. They found that in a 20° rise in temperature the reaction velocity increased about five-fold. This is the same order of magnitude as a two-fold rise for every 10° which characterizes most reactions in homogeneous systems. We may therefore conclude that in this case the diffusion through the reaction product is not the slow step nor the determining factor in governing the reaction velocity. On the other hand, their study of the reaction, $BaCO_3 + SiO_2$, gave temperature coefficients of the order of 1.67 for a 40° rise for the $BaCO_3 \cdot 10SiO_2$ mixture, 2.05 for 36° rise for the $BaCO_3 \cdot SiO_2$ mixture, and 2.46 for 40° rise for the $10BaCO_3 \cdot SiO_2$ mixture. These temperature coefficients are not only all low as compared with a two-fold increase every 10° (sixteen-fold for 40°), but they are also dependent on the mixing ratio of the component oxides. The temperature coefficients are of the order of those which we know correspond to diffusion processes. Their gradual rise as the proportion of $BaCO_3$ is increased is undoubtedly due to the fact that highly melting Ba_2SiO_4 is the principal reaction product, while the less stable $BaSiO_3$ is mainly formed when SiO_2 is in excess. We may therefore conclude that in this case the diffusion process through the reaction product is the rate-determining process for the whole reaction and, further, that the more stable and tightly bound Ba_2SiO_4 has a greater retarding influence than has $BaSiO_3$, which is in accord with the picture presented in an earlier paragraph. Summarizing these data we may say that the chemical processes at the phase boundary determine the reaction velocity in the case of CaO-MoO_3, but the diffusion velocity in $BaSiO_3$ or Ba_2SiO_4 is the slow process in the case of $BaCO_3$-SiO_2.

V. Effect of a Gas on the Reaction Velocity

A second mechanism may be mentioned which is not strictly a reaction process between two solids alone but which involves a gas phase. However, on account of its practical importance and the fact that small traces of gas may greatly accelerate such reactions, it should be given some attention.

In a certain sense the effect of a gas on the reaction between two solids is just the reverse of ordinary heterogeneous gas catalysis. Consequently, in the final analysis the facts and theories on adsorption and on rates of evaporation and condensation which have proved so useful in the study of heterogeneous gas catalysis may prove equally valuable in this reverse problem.

Cases may arise where a gas is produced as an intermediate stage in a reaction between two solids. For example, the reaction $Ag_2O + Zn \longrightarrow 2Ag + ZnO$ might be written $Ag_2O \longrightarrow 2Ag + {}^1/_2O_2$ and $Zn + {}^1/_2O_2 \longrightarrow ZnO$.

Such a reaction might prove to be a rapid one if the rates of evaporation and condensation of

oxygen are rapid. Roy S. Maize and the writer have been studying the conversion of amorphous alumina to corundum at temperatures from 850 to 1000°C. The amorphous alumina was prepared by calcination of aluminum nitrate at 400°C. At 850° the conversion is extremely slow (less than 10%). When 2% CaF_2 is added, a conversion of nearly 100% alumina is effected in 20 hours. The eutectic in the system CaF_2–Al_2O_3 is at 1260°C, approximately 400° above the reaction temperature, so it is highly improbable that any liquid phase is present. This reaction is being given further study. It is quite possible that gaseous AlF_3 is formed as an intermediate step.

Jander has measured several reactions in the presence and absence of water vapor, other factors such as particle size being held constant. Expressing the data in the form $k = Ce^{-q/RT}$, Jander found, in the case of $BaCO_3 + SiO_2$, a 22-fold increase in C due to passing water vapor at 355 millimeters pressure over the reaction mixture. The "heat of loosening," q, shows no change. For the reaction $CaO + SiO_2$, an 8.5-fold increase in C due to water vapor was observed, but q showed no change. Stated in another way, at 927° a dry $BaCO_3$-SiO_2 mixture reacted 17% in two hours. The presence of 355 millimeters water-vapor pressure increased the conversion to 65% in the same period of time. Jander and Stamm[20] are of the opinion that the water vapor is adsorbed on the surface of the crystallites of reaction product, preventing their growth, and thus providing a large specific surface over which diffusion of the reactants can readily occur. This is, roughly speaking, a physical effect comparable to that of fine grinding. It is noteworthy that the heat of loosening (or the energy of activation) is unaffected by the treatment with water vapor. Neither H_2 nor NH_3 vapor had any effect on the rate constant, except where they reacted chemically. The adsorption of water vapor appears to be more or less specific in these cases.

VI. The Reaction Occurs at the Interface between Two Phases

A good deal of information has been gathered which shows that the reaction takes place only on the phase boundary, and that, if the reaction product is present only in traces, the reaction rate may be very slow. Hulett and Taylor[21] attempted to measure the dissociation pressure of HgO by means of the gas-saturation method. The method consists of passing a neutral or inert gas over the solid oxide at the desired temperature with different rates of flow and analyzing the gas for oxygen or oxygen and mercury. The reaction in this case is $2HgO = 2Hg + O_2$. At temperatures above the boiling point of mercury there will be no interface between the solid HgO and the liquid Hg. The reaction actually proceeds so slowly that the measured partial pressure of O_2 at 468°C was only 0.002 of the true equilibrium pressure. The duration of the experiment was 12 hours which should have been ample for the complete decomposition.

Frequently a dissociation reaction will start at some point where the crystal is deformed or mechanically strained; in other cases some foreign particle may serve as a nucleus for initiating the reaction. In any case, however, it is not to be expected that the reaction rate will keep on increasing for an indefinite period. Sooner or later so much of the material is consumed that the area of interface begins to decrease. The typical curve for the decomposition of a solid is autocatalytic in the beginning, reaches a maximum velocity, and then decreases. An excellent example of this is seen in the thermal dissociation of potassium permanganate crystals at 240°C.[22] When the volume of oxygen produced is plotted against the time a perfectly symmetrical S-curve is obtained with a maximum slope at 50% dissociation, *i.e.*, when the area of interface between reactant and product is a maximum. The whole reaction is complete in one hour at 240°C.

The practical application of these considerations lies in the inoculation of a reacting substance with some of the finely powdered reaction product. This has been done with considerable success in the conversion of cyanite to mullite,[23] and of quartz to cristobalite. It should prove very useful in bringing about many polymorphic inversions as well as in the synthesis of complex compounds from their compound oxides. The seeding of opal glasses to bring about devitrification is a closely related phenomenon. On the other

[20] W. Jander and W. Stamm, *Z. anorg. allgem. Chem.*, **190**, 65–78 (1930); *Ceram. Abs.*, **9** [11], 981 (1930).

[21] G. A. Hulett and G. B. Taylor, *Jour. Phys. Chem.*, **17**, 567 (1913).

[22] Hinshelwood and Brown, *Phil. Mag.*, **40**, 569 (1920).

[23] G. A. Bole, *Amer. Refrac. Inst. Tech. Paper*, No. 5 (1928).

hand, the elimination of any trace of residual lime in the manufacture of tricalcium silicate would inhibit the dissociation $3CaO \cdot SiO_2 \longrightarrow 2CaO \cdot SiO_2 + CaO$ which ordinarily occurs between 1300°C and 1100°C.[24]

VII. Activity Increase Due to Crystal Transition, Etc.

We can not leave the subject of solid-phase reactions without mentioning the striking results obtained by Professor Hedvall in connection with accelerated reactions at transition temperatures. When a crystal is undergoing structural rearrangement the whole lattice is in an unstable condition and an opportunity is thereby offered for another substance to diffuse in and form new compounds. The effect persists over some temperature range. The following data show this clearly.

TABLE II

RELATION BETWEEN REACTION TEMPERATURE (R.T.) AND TRANSITION TEMPERATURE (T.T.)

	R. T.	T. T. ($AgNO_3$)
$BaO + AgNO_3$	170	160
$SrO + AgNO_3$	172	160
$CaO + AgNO_3$	164	160
$BaO + Ag_2SO_4$	342	411
$SrO + Ag_2SO_4$	422	411
$CaO + Ag_2SO_4$	422	411
$BaO + AgI$*	146°	146°
	170° (max. velocity)	

* W. Biltz, *Z. anorg. allgem. Chem.*, **197**, 399 (1931).

If ferric oxide is heated together with quartz under such conditions that the former is not decomposed, the reaction may go in two directions and in both cases it is affected by the inversion of quartz. Reaction 1 begins at 575° at which alpha quartz forms beta. There is a marked increase at about 950° when alpha quartz inverts to cristobalite. In all probability a compound is formed which has not yet been identified. Reaction 2 consists in the formation of a sort of solid solution with cristobalite. This substance is a beautiful rose color and probably part of the silicon atoms are replaced by iron. The lattice constant changes from 6.99 to 7.02. This reaction goes on only while the quartz is changing to cristobalite. Cristobalite itself does not react with Fe_2O_3 and neither does tridymite at these temperatures. The author wishes to emphasize particularly how important the inversion process is for this reaction.

[24] E. T. Carlson, "The Decomposition of Tricalcium Silicate in the Temperature Range 1000–1300°C" (see footnote 15).

VIII. Polarization or Deformation Influences

Since halide ions are easily polarized or distorted by the cation in the crystal the effect of the cation will be evident, leading to a wide range of temperature for the onset of the reaction of a halide series with a given oxide, *e.g.*,

$BaO + MX$

For $PbCl_2$	273	For $PbBr_2$	248	For PbI_2	200
For $NiCl_2$	325	For $NiBr_2$	272	For NiI_2	342

IX. Conductivity and Reactivity

Conductivity increases in a crystal when the ionic forces weaken, hence increase in conductivity should parallel increase in reaction.

$BaO + MX$ where MX = CuCl or CuI

Reaction Temp.	Temp. of rapid increase of halide conductivity
CuCl, ca 265	ca 260
CuBr, ca 290	ca 290
CuI, ca 340	ca 350

X. Practical Applications

No one can predict the development which may follow upon an intelligent application of the methods and principles of solid-phase reactions. Many commercial processes at the present time involve such reactions. Patents have been granted for new processes based essentially on such reactions. Thus in firing olivine with magnesite, magnesium ferrite is formed which acts as a bond in the olivine refractory.

Two factors probably stand out as most effective: one is fine grinding, and the other is intimate contact. The value of fine grinding is clearly shown by the experience of E. H. Fritz[25] in the manufacture of electrical porcelain. Finer grinding of feldspar led to more rapid vitrification and increased the firing range of the body, which considerably simplified the problem of getting complete vitrification throughout the kiln without overfiring parts of it. With regard to the problem of getting good physical contact, it is the experience of many workers that dry pressing is not as satisfactory as a wet process. The de-airing of wet clays in the pug mill has led to much denser and better vitrified ceramic bodies than formerly because it has increased the area of contact between the grains and reduced the total voids. Special attention should be given to the slip-casting process in this connection. When the

[25] E. H. Fritz, "Developments and Trends in the Heat Treatment of Electrical Porcelain," Symposium on Heat Treatment, Pennsylvania State College, October, 1933.

slip is properly deflocculated and the fine particles are dispersed, the total increase in surface area is enormous. A good deal of entrained air is removed as well. The best technique would appear to be deflocculating and casting, drying to a leathery texture, and then pressing to exact shape. This procedure is meeting with success in the production of high-grade refractories for special purposes. Undoubtedly its application to glass tank blocks and similar products is giving a denser body into which glasses and slags can not penetrate.

The use of inoculating agents to bring about crystallographic inversions is well illustrated by the use of raw cyanite to accelerate the alteration of clay to mullite. Cyanite inverts at a lower temperature than clay, and when well ground it produces a large number of nuclei of mullite which act as growth centers for the kaolinite⟶mullite transformation. Calcined cyanite would be of relatively little value here since the reaction runs fastest when the mullite nuclei are small, imperfect, and rich in surface. The perfection of the crystal form by calcining at a high temperature produces a relatively inert product which does not bond readily.

Finally it may be emphasized that proper consideration of solid-phase reactions may so stabilize refractories, tile, and heavy clay products that the slow changes occurring in long service at high temperatures or due to weathering are largely anticipated in the manufacture.

What is urgently needed in the ceramic field is a more complete knowledge of polymorphism of oxides, silicates, and similar materials, and of the means for effecting rapid transitions. This knowledge can only come by applying the most refined techniques of the physico-chemical laboratory to these problems.

Department of Ceramics
Pennsylvania State College
State College, Pennsylvania

ELECTROLYTIC REACTIONS IN VITREOUS ENAMELS AND THEIR RELATION TO THE ADHERENCE OF ENAMELS TO STEEL*

By Homer F. Staley

ABSTRACT

All the metals between iron and copper in the electromotive-force series of metals are plated out of solution during the firing of sheet-steel ground coats by the electrolytic action of the hot iron base. Of these plates, cobalt, nickel, and antimony promote adhesion, each of the following factors probably playing a part: (1) The plates of these metals adhere tenaciously to steel while enamel does not. (2) The coefficients of thermal expansion of these metals are intermediate between those of steel and those of commercial ground-coat and cover-coat glasses, thus giving a gradation of coefficients found desirable by Danielson and Sweely. (3) The enamel glass is mechanically bonded to the metal plate by dendrites, aided by any jagged projections and holes. (4) These metal plates are insoluble in the molten enamel; thus any structure favorable to adhesion, once formed, remains.

I. Introduction

All enamel technologists have been greatly interested in the excellent series of articles dealing with the mechanics of enamel adherence published during the past several years by R. M. King[1] and his co-workers. The researches reported in these various articles are considered by the writer to be of fundamental importance to the progress of enamel technology.

On reading these articles it seemed possible that the formation of the dendrites observed in ground-coat enamels on sheet steel was due to electrolytic reaction between the hot iron and the cobalt or nickel compounds dissolved in the enamel.

The reasons for this supposition were as follows: (*a*) As stated by King and his co-workers,[2] dendrites represent the form in which metal

* Presented at the Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February 14, 1934 (Enamel Division). Received March 13, 1934.

[1] Papers on "Mechanics of Enamel Adherence":
(*a*) J. O. Lord and W. C. Rueckel, I, *Jour. Amer. Ceram. Soc.*, **14** [10], 777–81 (1931); W. C. Rueckel and R. M. King, II, *ibid.*, pp. 782–88; W. K. Carter and R. M. King, III, *ibid.*, pp. 788–94.
(*b*) A. McK. Greaves-Walker and R. M. King, IV, *ibid.*, **15** [9], 476–80 (1932); G. H. Spencer-Strong and R. M. King, V, *ibid.*, pp. 480–83; K. Schwartzwalder and R. M. King, VI, *ibid.*, pp. 483–86; G. H. Spencer-Strong, J. O. Lord, and R. M. King, VII, *ibid.*, pp. 487–90.
(*c*) R. M. King, VIII, *ibid.*, **16** [5], 232–38 (1933).

[2] *Jour. Amer. Ceram. Soc.*, **15** [9], 488 (1932).

normally crystallizes from molten metal, aqueous solution, or any nonmetallic liquid which holds compounds of the metal in solution.

(*b*) Cobalt and nickel are below iron in the electromotive-force series of metals. Therefore, if electrolytic reactions take place in vitreous enamels they would normally be precipitated from enamels in which their salts are dissolved when in contact with metallic iron at temperatures high enough to bring enamels to the liquid phase. While the difference in potential between iron and cobalt or iron and nickel is not sufficient to produce a rapid plating action from solutions at atmospheric temperatures, the action increases with increase in temperature and should be very rapid at the elevated temperatures used in enameling.

(*c*) The well-known fact that, in firing cobalt-bearing ground coats, the blue color of cobalt oxide in solution fades and the green color of ferrous oxide in solution grows in intensity leads to the conclusion that cobalt oxide is disappearing from the enamel and iron oxide is coming into solution in the enamel. The disappearance of the cobalt oxide from the enamel in conjunction with the formation of dendrites is noted by King and his co-workers.[3] "The enamel near the crystals appeared light to dark gray in color, having lost the blue tinge still present in the remainder of the enamel."

(*d*) Manganese oxide did not produce dendrites or any other form of metallic precipitate. Manganese is above iron in the electromotive-force series and consequently can not be precipitated from solution by metallic iron.

(*e*) King and his co-workers stated rather tentatively that the dendrites consisted of alpha iron, but owing to the extreme minuteness of the particles studied and the heterogeneity, chemical and physical, of ground-coat enamels near the base metal, this statement seemed subject to possible revision. Definite proof that in enamels containing cobalt and nickel oxide some or all of the dendrites consist of iron would not exclude the possibility of electrolytic origin. The differences of potential between these metals and iron are so small that it is quite possible that cobalt and nickel could be precipitated at high temperatures and on cooling go into solution precipitating metallic iron. Slow cooling over a period of twenty-four hours, such as employed by King[4] in producing the largest crystals, would greatly facilitate this hypothetical reaction.

The writer did some work on the assumption that in ordinary blue ground coats cobalt and nickel were precipitated as metal by electrolytic reaction with iron. These views were presented in an oral discussion at the 1933 Meeting of the American Ceramic Society, but the proof, based on chemical analyses, was justly not considered convincing. Therefore, the following simple experiments were performed to prove the value of the theory.

II. Work with Water-Soluble Enamel

The properties of the common metals, assembled from various sources, are shown in Table I. Only compounds in solution of those below iron in the electromotive-force series could be expected to be precipitated by electrolytic reaction with metallic iron. Compounds and oxides of metals below copper are excluded by the fact that they are decomposed by heat alone. Therefore, the experiments were confined to compounds of metals between iron and copper.

III. Data Obtained with Water-Soluble Enamel

Since it seemed difficult to dissolve ordinary enamels from steel by acids or other chemicals without the probability of also removing some or all of any thin film of precipitated metal, a water-soluble enamel was used, consisting entirely of fused borax glass. Sufficient of a compound of the various metals to give 2 parts of the oxide of the metal was ground dry with 100 parts of the fused borax glass. Enough of each of the resultant mixtures to give a thickness of approximately $^1/_{16}$ inch of fused glass was placed in a flat-bottomed steel pan and fired at 1450°F for 5 minutes and allowed to cool in air. The enamels were then removed by immersion in boiling water for 8 hours.

The surfaces of the metal freed from enamel were examined under a microscope at magnifications of 100, 225, and 500 diameters. Using the 500-diameter magnification, indications of dendritic growths were determined on the surfaces of the specimens that had previously been coated with enamels containing cobalt oxide, nickel

[3] *Jour. Amer. Ceram. Soc.*, **15** [9], 484 (1932).

[4] *Ibid.*, p. 485.

oxide, and copper oxide. The results at 100 diameters were most instructive in regard to the general character of the surfaces since the area actually under observation was about $^1/_{16}$ inch in diameter. When using high magnifications, the area seen is really only a point and is liable to lead to wrong deductions. The results are shown in Table II.

TABLE I

PROPERTIES OF METALS

Metal	Electromotive-force series	Melting point (°C)	Coefficient of expansion (linear × 10^{-6})	Alloy with iron (?)
Magnesium		651	29.80	Yes
Aluminum	−1.27	659	31.50	Yes
Manganese	−1.07	1260		Yes
Zinc	−0.76	419	26.28	Yes
Chromium		1615		Yes
Cadmium	−0.42	321	31.60	
Iron	−0.43	Steel 1375	14.20	
Cobalt	−0.29	1480	12.36	Yes
Nickel	−0.23	1452	13.46	Yes
Tin	−0.14	232	22.57	Yes
Lead	−0.13	327	25.08	No*
Antimony	+0.19	630	12.00	Yes
Arsenic	+0.32	Subl. 556	3.86	Yes
Bismuth	+0.33	271	13.45	No*
Copper	+0.34	1083	16.07	Yes
Silver	+0.80	960	17.04	No*
Platinum	+0.86	1755	8.99	Yes
Gold	+1.00	1063	14.3	Yes

* Two immiscible liquid phases.

Comments on the results are hardly necessary. Comparing (2) with (3), it is evident that the solvent action of molten enamel on steel is to attack the corners first thus converting an irregular surface with angular projections into an irregular surface with rounded projections. Numbers (3), Bi_2O_3 addition, and (10), PbO addition, show the type of surfaces that would be expected from the deposition of fused metals which are incapable of forming alloys with iron. Numbers (4), SnO_2 addition, (5), Sb_2O_3 addition, and (7), As_2O_3 addition, show the effect of the formation of an alloy of iron with a low melting point metal. The presence of any arsenic is remarkable, but was confirmed by chemical test. Numbers (6), CuO addition, (8), Co_3O_4 addition, and (9), Ni_2O_3 addition, show definitely the formation of a metal plate on the surface of the steel. In the case of (6), that the plate consists of metallic copper is beyond question. Chemical tests showed the presence of metallic cobalt in (8) and metallic nickel in (9). They also showed the presence of metallic iron since it was not possible to separate the thin plate either chemically or mechanically without contamination by the underlying steel.

That all the surfaces were entirely free from any evidence of an oxide of iron layer is noteworthy. This in no way detracts from the value of Cooke's[5] basic discovery that the presence of a thin film of oxide of iron on steel is essential to produce wetting and uniform covering of the steel surface by the melting enamel.

The smoothness of the surfaces previously coated with enamels containing metallic oxides is in accord with King's observation[6] that the contact line of metal and ground coat becomes more smooth with addition of cobalt oxide to the ground coat. The metals deposited from the enamel solution seem to fill up the hollows first and thus tend to produce a smooth surface.

TABLE II

APPEARANCE OF PLATES AFTER ENAMEL WAS DISSOLVED OFF (magnification 100×)

No.	Oxide addition 2%	Description of surface
(1)	None	Pickled steel before enameling; irregular surface cut up into angular areas by rather sharp-edged crevices; numerous blocks projecting above general surface
(2)	None	Uneven surface made up of little rounded hills and valleys; bright metallic
(3)	Bi_2O_3	Similar to 2, but hills and valleys more angular and many semiglobular holes, like half bubbles, with smooth surfaces; bright metallic
(4)	SnO_2	Alligator hide effect, deep narrow creases with rounded edges; bright metallic
(5)	Sb_2O_3	Fairly smooth, but with many rough-edged irregular pits and numerous areas with fernlike or spongy appearance
(6)	CuO	Rough porous plate of metallic copper all over piece, very many rough-edged pits and crevices; bright metallic
(7)	As_2O_3	Porous structure with many roundish pits; bright metallic
(8)	Co_3O_4	Surface fairly smooth, but with very many irregular holes and pits; bright metallic
(9)	Ni_2O_3	Similar to (8), possibly not as many holes and pits; bright metallic
(10)	PbO	Porous, many holes, some round, some irregular; bright metallic

IV. Work with a Commercial Ground Coat

Taking a high-grade commercial ground coat, all of the coloring oxides were omitted. When milled and fired in the regular manner to normal maturity, this enamel gave a transparent light

[5] R. D. Cooke, *Jour. Amer. Ceram. Soc.*, **7** [4], 277–81 (1924).

[6] *Jour. Amer. Ceram. Soc.*, **14** [10], 787 (1931).

green glass through which the underlying clean steel could be seen. When badly overfired, the glass simply became a darker green in color. It was not until the enamel had been burned up and largely volatilized that black spots appeared. Evidently no black iron oxide layer is produced in commercial enamels simply by solution or solution and redeposition of iron from the surface of the steel. This is in accord with the findings of many investigators.

Taking the same colorless glass batch, 2% of oxide of copper was added. The frit was a robin's egg blue. When this frit was milled as an enamel with the customary mill additions and fired as a glaze on a porcelain-resistance coil tube, it gave a light blue glaze. When material from the same mill was applied to steel as an enamel and fired in the regular commercial manner to normal maturity, it gave a smooth mahogany-brown ground coat with tinges of blue on the surface and with fair adherence. On breaking off part of the enamel, it was found that the coating on the steel consisted of three parts: (1) next to the steel, a uniform plate of bright metallic copper with a few specks of dark brown "enamel" imbedded in or adhering to it; (2) as an intermediate section, a layer of dark brown "enamel" of semivitreous luster; and (3) as a top section, a layer of transparent blue-green glass.

The writer believes that this is a duplicate of the normal blue ground coat with its three layers: metal, "black oxide" layer, and more or less blue transparent top layer. The only difference is that copper oxide is functioning in place of cobalt or cobalt and nickel oxides. Owing to the ease with which copper can be identified, in comparison with the difficulty of distinguishing between metallic cobalt or metallic nickel and iron, this coating is an admirable object lesson.

There seems to be no question that the copper was deposited by electrolytic reaction between the metallic iron and the copper oxide or other copper compound in solution in the molten enamel. Every circumstance of its deposition conforms to what is commonly accepted as electrolytic reduction. Whether electrolytic reduction is really contact reduction or whether all contact reductions are electrolytic reductions are academic questions that must be left to the decision, if any is possible, of theoretical chemists. Incidentally, if electrolytic reduction of metallic compounds takes place in molten enamels, it means that these metallic compounds in molten enamels are more or less ionized, for electrolytic reactions can not take place in the absence of ionization.

The metallic deposits and other profound changes of surface noted in Table II with glasses containing metallic oxides are believed to be due to precipitation of the various metals by electrolytic reaction with iron. Undoubtedly all of these metals as well as copper react in the same way in commercial ground coats. This, of course, explains how cobalt and nickel can be precipitated as metals from commercial ground coats. As stated in the introduction, it is possible that on slow cooling these metals might be redissolved in part and replaced by a chemically equivalent amount of metallic iron. In either case the first layer of a blue ground coat consists of a metallic layer plated onto the surface of the steel by electrolytic action.

In order to determine the nature of the brown intermediate layer, an especially heavy coat was fused onto steel and from this large chips were broken off and examined under the microscope in cross-section at 225 diameters. The brown material was found to consist of a continuation of the metallic copper plate found adhering to the steel. In the upper part it contained isolated granules of enamel glass and, of course, the whole top was covered with enamel glass. The top of the plate was quite irregular with numerous jagged cavities and projections. The cavities were filled with transparent blue enamel. Numerous large dendrites could be seen. The brown color is due to the optical effect of a combination of transparent light blue glass with the color of metallic copper. Evidently when studying the specimens made with a water-soluble enamel we were looking down on the top of a structure similar to this but from which the enamel had been dissolved.

The top layer consisted of bluish-green transparent glass. In this connection it may be said that there are only two parts to a ground coat containing reducible metals: a top glassy section and beneath this a layer of precipitated metal. The so-called "black oxide layer" in a blue ground coat consists of precipitated metal coated with blue glass. The contact of this plated metal with the enamel glass constitutes the enamel-metal contact line shown in microphotographs.

Knowing what happens to cobalt in a blue ground coat, reference is made to an observation

made by Poste[7] as follows: "I have tried experimentally to leave out nitrates in a ground coat having nitrates in the formula. As a result, metallic cobalt, actually identified chemically, plated out on the steel stirring rod used in stirring the smelt in the crucible." Obviously a well-melted blue ground coat being fused onto sheet steel corresponds to Poste's stirring rod and batch without niter.

V. Conclusions

All the metals between iron and copper in the electromotive-force series of metals, if dissolved in glasses, are plated out of solution, when the glasses are fired as sheet-steel ground coats, by the electrolytic action of the hot iron base.

Of these plates cobalt, nickel, and antimony[8] promote adhesion, each of the following factors probably playing a part:

(1) The plates of these metals adhere tenaciously to steel while enamel does not.

(2) The coefficients of thermal expansion of these metals are intermediate between those of steel and those of commercial ground-coat and cover-coat glasses, thus giving a gradation of coefficients found desirable by Danielson and Sweely.[9]

(3) The enamel glass is mechanically bonded to the metal plate by dendrites, aided by any jagged projections and holes.

(4) Since these metal plates are insoluble in the molten enamel, any structure favorable to adhesion, once formed, remains.

[7] E. P. Poste, "Discussion on Effect of Muffle Atmosphere in Firing Enamels," *Bull. Amer. Ceram. Soc.*, **3** [11], 440 (1924).

[8] Antimony is probably present alloyed with iron.

[9] R. R. Danielson and B. T. Sweely, *Jour. Amer. Ceram. Soc.*, **6** [10], 1011 (1923).

METAL & THERMIT CORPORATION
NEW YORK, N. Y.

A FURTHER PROGRESS REPORT ON THE STUDY OF GASES IN ENAMELING IRON*

BY A. N. LUCIAN[1] AND KARL KAUTZ[2]

ABSTRACT

Spectrographic analyses were made of the gases evolved when enameling iron, ground-coat enamel, and iron enameled in ground coat were heated *in vacuo* at various temperatures. Below 1200°F the gases from enameling iron contained hydrogen, water vapor, carbon monoxide, carbon dioxide, and nitrogen. Between 1200°F and 1600°F, the gases from enameling iron contained carbon monoxide, carbon dioxide, and nitrogen. The gases from dried ground-coat enamel slip at temperatures not exceeding 1600°F consisted principally of water vapor. The gases from ground-coat enameled iron (reboiling gases) contained hydrogen, water vapor, carbon monoxide, carbon dioxide, and nitrogen.

I. Introduction

Difficulty is encountered in attempting to analyze the gases that cause reboiling. The quantity of gases evolved is extremely small; hence, to analyze the gases volumetrically or by absorption, using chemical methods, requires the treating of a large quantity of enameled iron in such a manner that a measurable volume of gas results. If, however, the enameled iron is heated *in vacuo*, the small amount of gases evolved can readily be sealed off in a Plücker spectrum tube at sufficient pressure to produce a brilliant discharge. The gases can then be analyzed by means of a spectroscope or spectrograph.

The gases evolved from enameling iron and from ground-coat enamel when heated can be analyzed in a similar manner. Thus by direct comparison of the analyses the source of reboiling gases may be indicated.

II. Preparation of Spectrum Tubes

(1) Tubes for Gases from Iron The apparatus used in obtaining the gases from iron consisted of an inductively heated quartz tube vacuum furnace into which the samples could be brought to the desired temperature. The vacuum in this furnace was obtained by means of a two-stage mer-

* Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Cincinnati, Ohio, February, 1934 (Enamel Division). Received February 15, 1934.

[1] Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pa.

[2] Republic Steel Corporation, Massillon, Ohio.

cury diffusion pump backed by a Cenco-Megovac oil pump through traps and drying tubes. The diffusion pump was connected to the quartz-tube furnace by means of a glass line containing a liquid air trap, a spectrum-tube manifold, and a precision McLeod gage for accurately measuring the pressures obtained. The spectrum tubes were sealed to the manifold of this apparatus. Great care was taken to secure a black vacuum (no discharge through spectrum tubes) in the system before heating the iron. All water vapor was driven out of the system by carefully flame heating the metal, quartz, and glass parts, including the spectrum tubes. An induction coil discharge, the polarity of which was frequently reversed, was passed continuously between the electrodes of the spectrum tubes during this torching operation. In this way absorbed gases and water vapor clinging to the inner walls of the system and occluded gases in the metal electrodes were freed and removed by the pumps.

When a vacuum of 0.001 micron or less was obtained, the iron samples (reboiling stock) were slowly heated. By means of a stopcock, suitably placed in the line, the evolved gases were allowed to accumulate in the quartz system and spectrum tubes. At 1200°F the stopcock was partially opened and some of the gases pumped out of the system until the spectrum tube had the correct pressure for a discharge of maximum intensity. This usually occurred when three or four striations in the positive column and a Crookes' dark space of less than one centimeter were visible. One spectrum tube was then sealed off with a gas torch. The stopcock was opened wide and the accumulated gases reduced to a very low pressure, after which it was closed, gases evolved between 1200°F and 1600°F were collected, and a spectrum tube was sealed off. In like manner, the gases evolved from the iron between 1600°F and 2000°F were obtained.

(2) Tubes for Gases from Enamel Spectrum tubes were made of the gases evolved from dried ground-coat enamel slip heated in a vacuum, using an apparatus similar to that described above, comprising, however, a smaller quartz tube heated by means of a Hoskins type FD-208 electric furnace.

A 25-cubic centimeter Vitreosil crucible filled with ground-coat enamel slip and dried to constant weight at 300°F was placed near the closed end of the quartz tube. The same precautions to free the system of water vapor and occluded electrode gases were taken as in collecting the iron gases. Spectrum tubes of the gases evolved from the dried enamel slip were sealed off at 1300°F, 1500°F, and 1600°F, in a manner as described above. The fused enamel resulting from this treatment appeared clear and homogeneous, and no gas bubbles could be detected with a microscope.

(3) Tubes for Gases from Enameled Iron Before obtaining spectrum tubes of reboiling gases, it was necessary to determine whether the gases evolved caused reboiling when enameled iron (reboiling stock) was heated *in vacuo*. If so, then collection and analysis of reboiling gases could easily be accomplished.

A piece of enameled iron, $1^3/_4$ by $3^1/_2$ inches, was placed in the quartz tube and the glass cap cemented in place and sealed to the vacuum pumps. The enameled sample was kept in the cold portion of the quartz tube outside the furnace while the empty closed end was allowed to soak at 1500°F under a vacuum well below five microns. The quartz tube and contents were then sealed off from the vacuum pumps, removed from the furnace, and the enameled-iron sample dropped into the heated end. This was immediately placed back into the furnace for 40 seconds, removed, and the enameled-iron sample allowed to fall back into the cold end again.

Enameled iron does reboil in vacuum; but unlike the normal blisters occurring at atmospheric pressure, the enamel had frothed or foamed badly, evidently due to a violent evolution of gases. Some bubbles were $^1/_2$ inch in diameter and varied in size down to normal reboil blisters.

The problem then of preparing spectrum tubes of reboiling gases became quite similar to the problem of preparing spectrum tubes of enamel gases and the same apparatus was used. A pack of 18 ground-coat enameled-iron samples (reboiling stock) spaced with No. 18 nickel wire was placed in the quartz tube and sealed vacuum tight to the pumps. The manifold arm carried three spectrum tubes. The same precautions of freeing the tubes and system of water vapor and occluded electrode gases were taken, as previously described. Tubes were sealed off at 1300°F, 1400°F, and 1500°F.

III. Spectrum Tubes of Standard Gases

Spectrum tubes of the following gases were obtained from various commercial supply houses: hydrogen, helium, argon, oxygen, nitrogen, air, water vapor, sulfur vapor, mercury vapor, nitric oxide, carbon monoxide, and carbon dioxide. The spectrograph revealed impurities in most of these tubes making them unfit for spectroscopic standards. The hydrogen tubes contained water vapor, the oxygen contained nitrogen, and very little difference could be detected between nitrogen, air, and nitric oxide. A comparison of three carbon monoxide and three carbon dioxide tubes showed essentially similar spectra.

A preliminary examination of the spectrum tubes of the gases from iron, ground-coat enamel, and enameled iron revealed, fortunately, only water vapor, hydrogen, nitrogen, and carbon monoxide or dioxide as the essential constituents. The commercially obtained water vapor and hydrogen tubes could be used as spectroscopic standards although the hydrogen tubes did contain traces of water vapor; but to obtain a reliable standard of carbon oxide band spectra, tubes containing CO and CO_2 in a purified condition had to be prepared. This was done by exhausting spectrum tubes attached to a vacuum system, carefully eliminating water vapor and occluded electrode gases, until a black vacuum was attained. Purified gas was then admitted to the system, the pressure adjusted to the proper amount for maximum intensity of discharge and the tubes sealed off with a gas torch. Carbon monoxide was obtained by the action of concentrated chemically pure sulfuric acid upon concentrated chemically pure formic acid. This was purified by passing through a tube filled with ascarite (mixture of sodium hydroxide and asbestos) to remove carbon dioxide, then through tubes containing dehydrite (magnesium perchlorate trihydrate), then phosphorus pentoxide to remove water vapor, and finally through a liquid air trap to freeze out traces of water vapor, carbon dioxide, sulfuric acid, or formic acid remaining.

Dry ice or solid carbon dioxide was used as the source of carbon dioxide. This was freed of water vapor by passing through tubes of dehydrite and phosphorus pentoxide and finally through a trap cooled with a mixture of ether and solid carbon dioxide.

Before discussing the spectra of gases obtained from iron, ground-coat enamel, and enameled iron, it might be well to call attention to some difficulties encountered in attempting to identify or rather to distinguish between the spectra of diatomic and triatomic molecules such as CO and CO_2. It is common knowledge, of course, that molecular spectra consist generally of systems of bands rather than lines, and the structure of the band systems becomes more complicated as the number of atoms in the molecule increases.

Referring particularly to the spectra of CO and CO_2, modern spectroscopists[3] recognize the fact that it is a rather simple matter to obtain the various characteristic bands of CO in a sealed spectrum tube (stagnant gas) when excited by ordinary electrical means. These bands include, in the visible region, the well-known Ångström bands, third position bands, etc. The prominent bands easily seen on the following plates clearly exhibit the Ångström bands. But to obtain the true band spectrum of CO_2 gas, one must ordinarily excite the gas while the gas is in a steady state of flow at low pressure. Under such a condition a characteristic and very complicated CO_2 spectrum is easily obtained. However, as soon as the flow of gas is stopped, the characteristic CO_2 bands disappear almost completely and the CO bands spring into view. Obviously in a stagnant condition, the CO_2 gas dissociates as follows: $2CO_2 \longrightarrow 2CO + O_2$, thus giving an ample supply of CO molecules. Under certain conditions not well understood at present, CO_2 in a stagnant condition may exhibit part of its characteristic bands. This is the reason for the construction of the CO_2 tubes described above. On the other hand, there is always the possibility of CO_2 existing in a spectrum tube filled with pure CO, since under the influence of the electric discharge the following reaction can take place: $2CO \longrightarrow CO_2 + C$.

The present investigation was practically limited to the stagnant-gas method of analysis, since the evolved gases were in such minute quantities that just enough gas to fill a few spectrum tubes could be obtained and these tubes were then sealed off the system. In the analysis of the spectrum plates, therefore, positive identification of the existence or nonexistence of carbon monoxide gas

[3] (*a*) Duffendack and Fox, *Astrophys. Jour.*, **65**, 214 (1927).
(*b*) H. D. Smyth, *Phys. Rev.*, **38**, 2000 (1931).

(CO) could be made without justifying statements as to whether the CO gas observed in the spectrum tubes was originally given off from the source in question as pure CO or as a mixture of CO and CO_2. However, as shall be pointed out later from chemical considerations, it is almost certain that carbon oxides given off from iron at an elevated temperature *in vacuo* and in contact with iron oxides must consist of a mixture of CO and CO_2.

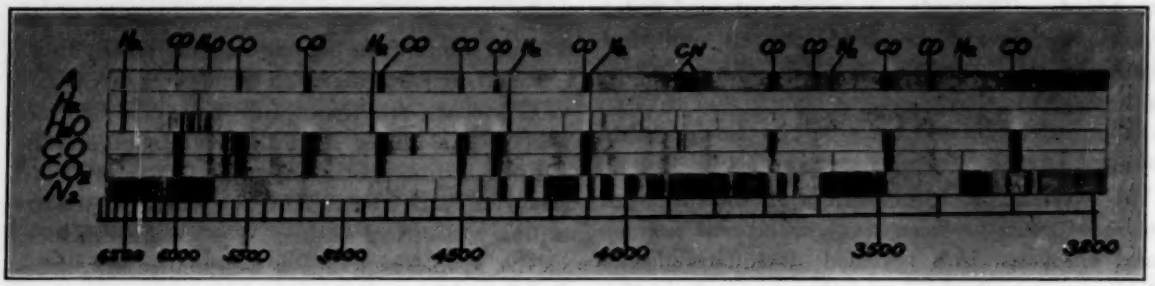

FIG. 1.—The spectrum of gases from iron at 1200°F (*A*) compared with the spectra of H_2, H_2O, CO, CO_2, and N_2.

IV. Apparatus and Procedure

Spectrographs of the various spectrum tubes were obtained with a Hilger large model quartz spectrograph set at position 1 (the visible spectrum from 8000 to 3000 Å). A slit opening of 0.05 millimeter and a slit length of 5 millimeters was used for all gas spectrum tubes. The capillary of the spectrum tube was placed one centimeter away from the slit and no condensing lens was used. The time of exposure varied from $12\frac{1}{2}$ to 30 minutes dependent upon the intensity of the discharge. The discharge through the tube was obtained with an induction coil of one-inch spark connected in series with a rheostat to a 6-volt storage battery.

Process Panchromatic plates, 4 by 10 inches, were used for the exposures and were developed in an Elon-hydroquinone contrast developer for 5 minutes at 70°F. All measurements for identification were made from the original plates with a comparator using an iron-arc scale. Prints were made duplicating the original plates and from these the spectra of Figs. 1 to 4 were assembled on cardboard. An approximate wave-length scale is shown with each figure.

V. Analysis of Spectra

(1) Gases from Iron

In Fig. 1 is shown the spectrum of gases from iron at 1200°F as compared with the spectra of hydrogen, water vapor, carbon monoxide, carbon dioxide, and nitrogen. An analysis of this spectrum shows the iron gases to contain hydrogen, water vapor, carbon monoxide, nitrogen, cyanogen, and possibly carbon dioxide.

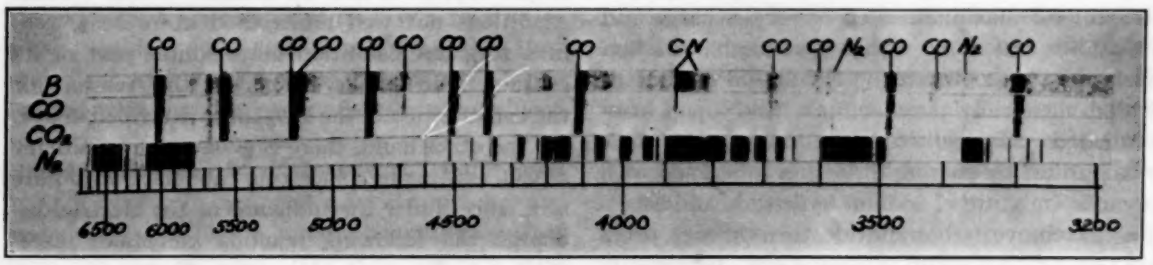

FIG. 2.—The spectrum of gases from iron between 1200 to 1600°F (*B*) compared with the spectra of CO, CO_2, and N_2.

The spectrum of the gases from iron between 1200°F and 1600°F is shown in Fig. 2. For comparison, the spectra of carbon monoxide, carbon dioxide, and nitrogen are also shown. An analysis of this spectrum shows no hydrogen or water vapor to be present and the gases are prepon-

derantly carbon monoxide and possibly carbon dioxide with traces of nitrogen and cyanogen.

(2) Gases from Enamel The spectrum of gases from ground-coat enamel at 1500°F is shown in Fig. 3, together with the spectra of water vapor and hydrogen. An analysis of this spectrum shows that it consists mainly of water vapor. A few lines in the violet end at about 3640 Å are believed to be due to cobalt.

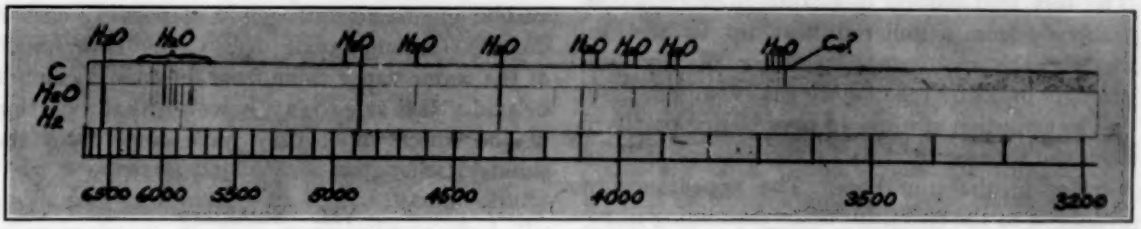

FIG. 3.—The spectrum of gases from ground-coat enamel at 1500°F (*C*) compared with the spectra of H_2O and H_2.

(3) Reboiling Gases The spectrum of reboiling gases at 1500°F is shown in Fig. 4 together with the spectra of water vapor, hydrogen, carbon monoxide, carbon dioxide, and nitrogen. An analysis of this spectrum shows that it consists principally of hydrogen, water vapor, carbon monoxide, and possibly carbon dioxide. Small amounts of nitrogen are also present.

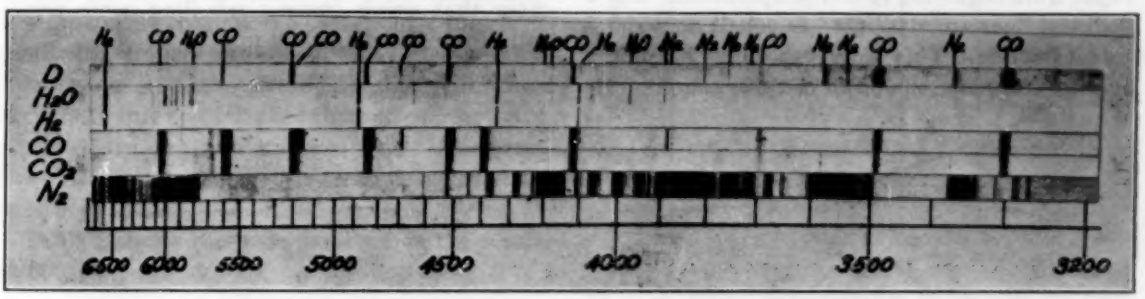

FIG. 4.—The spectrum of reboiling gases at 1500°F (*D*) compared with spectra of H_2O, H_2, CO, CO_2, and N_2.

VI. Discussion

During the preparation of the various spectrum tubes, the discharge was constantly observed and studied by means of a direct-vision spectroscope at various temperatures and pressures. It was noticed that as enameling iron was gradually heated *in vacuo*, the first spectra to appear were those of hydrogen and water vapor. At dull red heat the carbon oxide spectra started to appear and increased in brilliance as the temperature increased. The hydrogen-water vapor spectra started to diminish in intensity at about 1100°F and was completely gone at 1300°F. At higher temperatures only carbon oxide gases remained. This can be readily seen in Figs. 1 and 2.

The hydrogen obviously is occluded in the iron. Whether it became occluded in the open-hearth furnace when the iron was liquid or whether it was occluded in pickling operations prior to the vacuum heating is not known. The ease with which it leaves the metal when heated *in vacuo* seems to indicate atomic hydrogen in pickling as the source. The analysis of the spectra shows both hydrogen and water vapor present in the gases from iron at 1200°F. Since all commercial iron made in the open hearth under oxidizing conditions contains iron oxides, a portion of the occluded hydrogen liberated at high temperatures in a vacuum would thus be partially oxidized according to the reversible reaction

$$FeO + H_2 \leftrightarrows Fe + H_2O.$$

The carbon monoxide liberated in a vacuum above a red heat may have been occluded in the iron as such; it may have resulted from the decomposition of iron or manganese carbonyls, or from the chemical reaction between iron oxide and carbon

or iron carbide. With iron carbide the reaction is

$$Fe_3C + FeO \leftrightarrows 4Fe + CO.$$

The carbon monoxide liberated can be oxidized further to carbon dioxide by iron oxide, thus

$$FeO + CO \leftrightarrows Fe + CO_2.$$

The fact that carbon monoxide is evolved continuously from a dull red heat up to and including the melting temperature of the iron strongly indicates reactionary gas evolution.

The evolution of nitrogen may be due partly to occluded nitrogen and partly to decomposition of nitrides in the iron base. The appearance of cyanogen in the spectrum tubes containing nitrogen and carbon oxides seems to indicate a side reaction between these substances under the influence of the electric discharge.

It is believed that when enameling iron is heated above a red heat *in vacuo*, occluded hydrogen, reactionary carbon monoxide, and decomposed combined nitrogen are evolved, the first two reacting with iron oxides present to form small amounts of water vapor and carbon dioxide.

A study with a direct vision spectroscope of the gases evolved from dried ground-coat enamel slip during heating to 1600°F, showed only water vapor from beginning to end of operation. A few doubtful lines are attributed to cobalt or perhaps cobalt fluoride. This water vapor may have been evolved from any one or all of three sources: (1) dehydration of borax used for setting up enamel slip, (2) dehydration of clay used in milling, or (3) dehydration of hydrated particles of the frit.

A study of reboiling gases during their evolution was not attempted with a spectroscope. The spectrograph of reboiling gases, however, is similar to the gases evolved from iron at 1200°F. It shows the presence of hydrogen, water vapor, carbon monoxide, nitrogen, and possibly carbon dioxide (accompanying the CO). How much of the water vapor came from the enamel can not be said. It is safe to say, however, that a portion of the water vapor may have come from the enamel itself.

VII. Summary

The gases evolved from enameling iron up to and including 1200°F consist of hydrogen, water vapor, carbon monoxide (carbon dioxide), and nitrogen.

The gases evolved from enameling iron between 1200°F and 1600°F consist of carbon monoxide (carbon dioxide) and nitrogen.

The gas evolved from ground-coat enamel at 1500°F consists principally of water vapor.

The gases causing reboiling consist of hydrogen, water vapor, carbon monoxide (carbon dioxide), and nitrogen. The evidence given above indicates that gases causing reboiling come principally from the enameling iron.

Republic Steel Corporation
Massillon, Ohio

THE THERMAL CONDUCTIVITY OF REFRACTORIES*

By Gordon B. Wilkes

ABSTRACT

The thermal conductivity of recrystallized silicon carbide, clay-bonded silicon carbide, and silica and fireclay brick has been determined from 200 to 2600°F. The results are compared with those of previous investigators and a possible explanation of the peculiar variation of the coefficient of thermal conductivity with temperature for certain brick is given.

I. Introduction

In a previous paper,[1] the author described a method of determining the thermal conductivity of refractories at high temperatures, and the values for magnesite brick were given. Since that time, the thermal conductivity of a number of other common refractories has been determined in essentially the same apparatus.

II. Previous Investigations

In the case of fireclay and silica brick, there has been a considerable number of investigations, but the literature indicates a limited amount of work on recrystallized and clay-bonded silicon carbide brick. The better known values of the last twenty years that cover a sufficient range of temperature to show the variation of the coefficient with temperature are shown in Figs. 1 to 4 in comparison with the author's results. In these curves the true coefficient of thermal conductivity, expressed in gram-calories, seconds^{-1}, centimeters^{-2}, centimeters, °C^{-1}, is plotted against temperature in °C.

Table I shows the wide variation in the results at 900°C.

TABLE I

PUBLISHED VALUES OF THERMAL CONDUCTIVITY

(k = c.g.s. units at 900°C)

	Minimum	Maximum
Fire clay	0.0017	0.0040
Silica	0.0031	0.0054
Recrystallized silicon carbide	0.035	0.054
Clay-bonded silicon carbide	0.012	0.037

The great difference in values is doubtless in part due to difference in the samples tested, but it is impossible to check up this point due to lack of suitable descriptions of the brick. On the other hand, there are cases where the samples were furnished by the same manufacturer with the same brand name, and the values differ sufficiently to indicate probable errors in method.

III. Apparatus

The apparatus was essentially the same as used in the previous investigation of magnesite brick, consisting of a Globar resistance furnace, the bottom of which contained three of the samples under test. A water calorimeter and guard-ring were placed below the samples except when high mean temperatures were desired, when a layer of insulating brick was placed between the calorimeter and the samples. The furnace has been improved somewhat by the use of six $^5/_8$-inch Globar units with water-cooled holders in place of the nine $^1/_2$-inch units, air-cooled. Better thermal insulation has also been provided by the use of kaolin insulating brick.

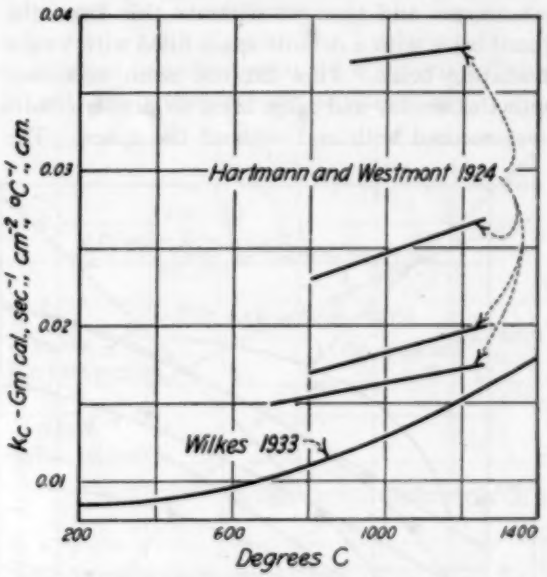

FIG. 1.—Thermal conductivity of clay-bonded SiC brick.

In the case of the recrystallized silicon-carbide brick, a differential platinum platinum–10% rhodium thermocouple was used, cemented in grooves on the hot and cold surfaces of the specimen. A separate couple was used to determine the actual temperature of the cooler surface. A "Type K"

* Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Cincinnati, Ohio, February 13, 1934 (Refractories Division). Received January 29, 1934.

[1] G. B. Wilkes, "Thermal Conductivity of Magnesite Brick," *Jour. Amer. Ceram. Soc.*, **16** [3] 125–30 (1933).

Leeds & Northrup potentiometer was used to measure the electromotive force.

With the better-conducting brick, it was found necessary to cut one brick to the exact size of the calorimeter and then to separate this from the guard brick with a definite space filled with kaolin insulating brick. This did not seem necessary with the fireclay and silica brick as similar results were secured with and without the space. The different treatment required is probably due to insufficient guarding in the case of the better-conducting brick.

Table II describes the materials tested. The bulk density and porosity were determined in the laboratory on the specimens tested, but the chemical analysis was given by the manufacturer as a typical analysis of the brick submitted.

TABLE II

DESCRIPTION OF SAMPLES

	Fireclay	Silica	Clay-bonded silicon carbide	Recrystallized silicon carbide
Trade name	Mexko	Star	Norton	Refrax
Manufacturer	A. P. Green Fire Brick Co.	Harbison-Walker Refractories Co.	Norton Co.	Carborundum Co.
Bulk density (lb./ft.$^{-3}$)	143	95	139	136
Porosity (%)	15.2	28.0	28.3	34.4
		Approximate chemical analysis (%)		
SiO_2	52.5	95.9	8.2	0.7
Al_2O_3	42.7	1.0	4.2	1.3
Fe_2O_3	1.6	1.0	0.3	1.3
CaO	0.5	2.0	0.2	
MgO	Trace	0.1		
TiO_2	2.0		0.2	
SiC			86.7	96.9
Alkalis	0.6	0.1	0.2	

IV. Results

A minimum of five runs was made on each type of brick with mean temperatures varying between approximately 250°F and 2400°F, and the hot-surface temperatures reaching 2650°F. The results of these tests were plotted on a chart showing the relation between mean temperature of the specimen and the coefficient of thermal conductivity.

From the curve of the mean conductivity, k_f

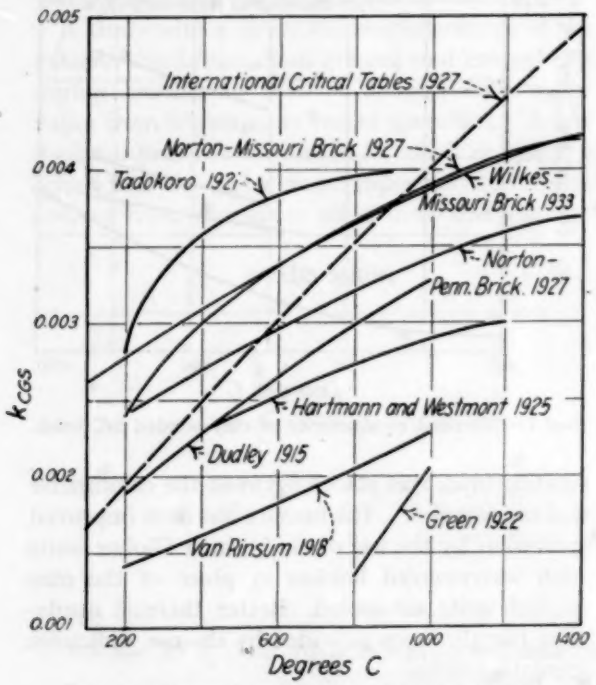

FIG. 2.—Thermal conductivity of fireclay brick.

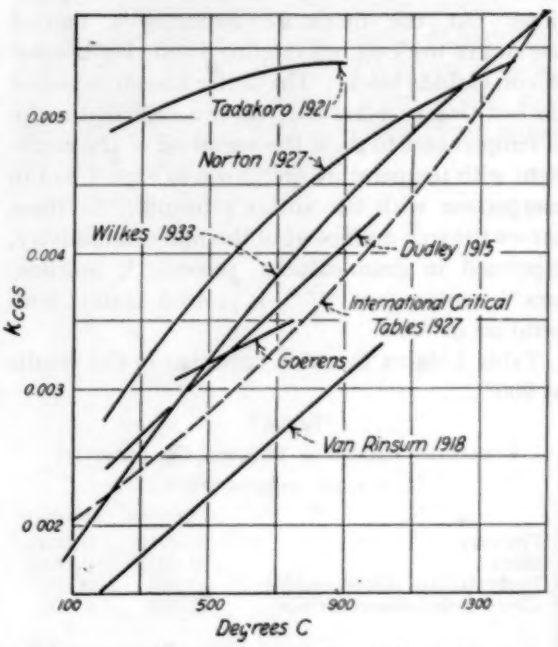

FIG. 3.—Thermal conductivity of silica brick.

versus mean temperature, the true k_f at any temperature, t, was calculated using the equation

$$\text{True } k_f = a + bt + ct^2$$

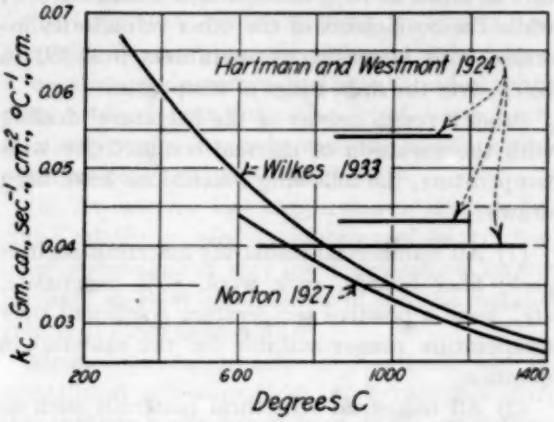

FIG. 4.—Thermal conductivity of recrystallized SiC brick.

where a, b, and c are constants and t is the temperature in °F.

Taking any one test point on the mean temperature curve, the following relation holds:

$$\text{Mean } k_f(t_2 - t_1) = \int_{t_1}^{t_2} \text{true } k_f dt = \int_{t_1}^{t_2} (a + bt + ct^2)dt.$$

With the suitable choice of three such points, the simultaneous equations for the values of a, b, and c may be solved.

The resulting equations showing the value of the coefficient of thermal conductivity expressed in British thermal units, hour^{-1}, foot^{-2}, inch, °F^{-1} at different temperatures in °F are given in Table III with the permissible temperature range.

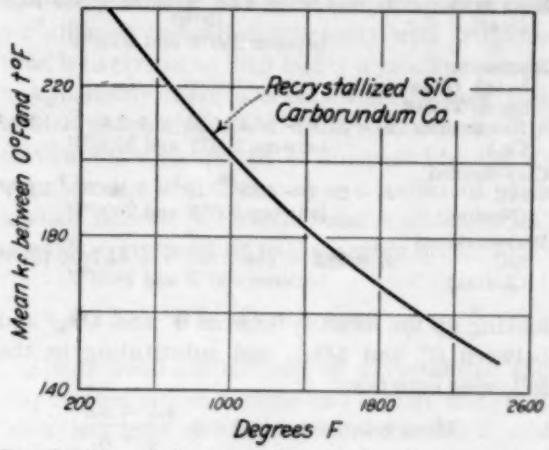

FIG. 6.—Mean k_f between 0°F and t°F of recrystallized SiC brick.

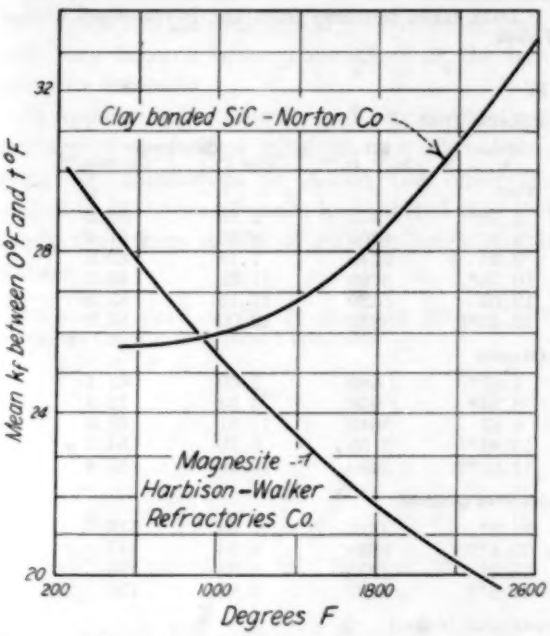

FIG. 5.—Mean k_f between 0°F and t°F of magnesite and clay-bonded SiC brick.

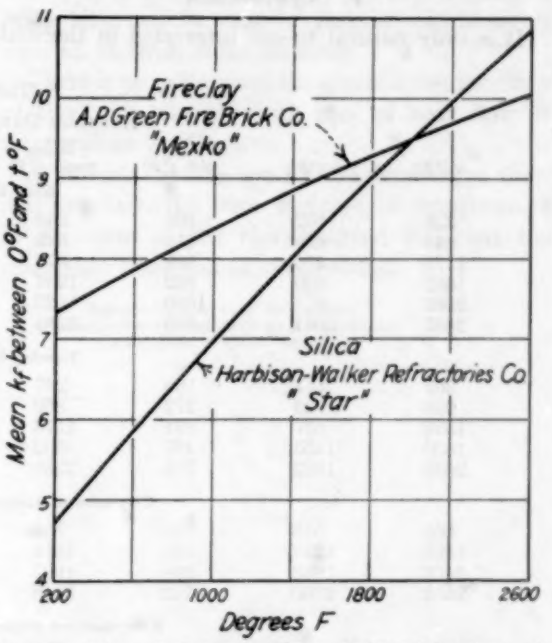

FIG. 7.—Mean k_f between 0°F and t°F of fireclay and silica brick.

The mean coefficient of thermal conductivity between any two temperatures may be calculated from the above equations, but it is much simpler to make use of a plot showing the mean coefficient between 0°F and t°F. The mean k_f between any two temperatures, t_2 and t_1, may then be found by

TABLE III

FORMULAS FOR THERMAL CONDUCTIVITY

Fireclay brick (Mexko)	$k_t = 7.03 + 2.87 \times 10^{-3}t - 0.31 \times 10^{-6}t^2$ between 200°F and 2650°F
Silica brick (Star)	$k_t = 4.06 + 6.20 \times 10^{-3}t - 0.575 \times 10^{-6}t^2$ between 200°F and 2650°F
Magnesite brick (Harbison-Walker Refractories Co.)	$k_t = 31.8 - 14.4 \times 10^{-3}t + 2.66 \times 10^{-6}t^2$ between 200°F and 2650°F
Clay-bonded SiC (Norton)	$k_t = 26.4 - 4.88 \times 10^{-3}t + 5.87 \times 10^{-6}t^2$ between 500°F and 2600°F
Recrystallized SiC (Refrax)	$k_t = 262 - 134 \times 10^{-3}t + 24.7 \times 10^{-6}t^2$ between 250°F and 2450°F

looking up the mean k_f between 0° and $t_2(k_2)$ and between 0° and $t_1(k_1)$, and substituting in the following equation:

$$\text{Mean } k_f \text{ between } t_2 \text{ and } t_1 = \frac{k_2t_2 - k_1t_1}{t_2 - t_1}.$$

Curves showing the relation of the mean k_f between 0°F and t°F for the different types of brick are shown in Figs. 5 to 7.

V. Speculation

It is only natural to one interested in thermal conductivity to wonder why, in the case of the magnesite and recrystallized silicon-carbide brick, the coefficient decreases with increasing temperature as much as 70% between 200°F and 2500°F, while the coefficients of the other refractories increase with increasing temperatures from 50 to 150% over the same range of temperature.

From a rough survey of the literature[2] dealing with the variation of thermal conductivity with temperature, the following conclusions have been drawn:

(1) All commercial insulating materials such as cork, fiber boards, rock wool, 85% magnesite, etc., have a positive temperature coefficient over temperature ranges suitable for the material in question.

(2) All industrial structural materials such as stone, brick, wood, concrete, etc., with the exception of metals and the two cases mentioned at the beginning of this section, have a positive temperature coefficient.

(3) The temperature coefficient of metals is, in

[2] Data taken primarily from the *International Critical Tables*.

TABLE IV

AVERAGE DATA FOR EACH TEST

t_2 (°F)	t_1 (°F)	Temp. dif. (°F)	Mean temp. (°F)	Mean k_f	B.t.u. hr.$^{-1}$, ft.$^{-2}$	Calorimeter Rise (°C)	Calorimeter Cc., min.$^{-1}$
			Silica brick (Star)				
328	162	166	245	5.52*	373	2.78	35.2
848	429	419	639	8.11	1390	4.48	81.4
1175	576	599	876	9.20	2240	7.15	82.6
1662	800	862	1231	10.78*	3790	11.62	85.8
2066	977	1089	1522	12.23	5420	17.13	83.3
2667	2061	606	2364	15.45*†	3820	12.00	83.8
			Fireclay brick (Mexko)				
307	147	160	227	7.67*	489	2.09	61.4
995	723	272	859	8.54†	958	3.34	72.9
1578	657	921	1118	9.87	3640	11.51	82.8
1850	1353	497	1602	10.83*†	2150	6.70	84.0
2653	1922	731	2288	11.97*†	3490	10.48	87.4
			Clay-bonded silicon carbide brick (Norton)				
865	545	320	705	25.6*	3210	7.08	119
1395	1234	161	1315	30.1*†	1880	4.24	117
2106	1888	218	1997	38.3†	3260	6.98	123
2532	2300	232	2416	49.8*†	4150	8.88	123
			Recrystallized silicon carbide brick (Refrax)				
271.0	259.5	11.5	265	228*	1100	4.73	61.5
549.0	514.3	34.7	532	194	2820	6.09	122
1477	1431	46	1454	124*†	2400	5.21	121
1585	1531	54	1558	118†	2670	5.62	125
1924	1843	81	1884	99.8†	3400	7.40	121
2458	2318	140	2388	81.8*†	5110	10.60	127

* Indicates runs used in calculating the constants a, b, and c.

† Indicates that insulating brick was placed between the calorimeter and the lower surface of the brick.

NOTE: If a plot is made of the data in Table IV for each brick showing relation between mean k_f and the mean temperature, it will be noted that the points all lie very close to a smooth curve drawn through them. Since the rate of heat flow (B.t.u. hr.$^{-1}$, ft.$^{-2}$) varies considerably in these tests, this indicates that the thermal conductivity does not vary appreciably with rate of heat flow or temperature gradient over the range covered.

general, relatively small and is sometimes positive and sometimes negative.

(4) Amorphous materials such as glass, asphalt, etc., have a positive temperature coefficient.

(5) Crystalline materials such as quartz, ice, etc., with the exception of metals and carbon, have a negative temperature coefficient, and there is some evidence that the coefficient of thermal conductivity varies inversely with the absolute temperature between 100°C and −190°C.

(6) At extreme low temperatures, crystals become relatively good conductors of heat. Sosman[3] states that at very low temperatures quartz becomes as good a conductor of heat as metallic gold is at room temperature.

Microscopic examination of magnesite and recrystallized silicon-carbide brick indicates that the materials are more than 99% crystalline. The variation of thermal conductivity with temperature for these two brick is similar to that of crystals, which become poorer conductors of heat as the temperature increases.

Microscopic examination of clay-bonded SiC and fireclay brick indicates 5% or more of glass, and they become better conductors as the temperature increases.

It apparently is difficult to determine the percentage of crystalline material in a silica brick, either by microscope or X-ray, but observers, skilled in this type of work, have stated that it is likely that there is 5% of glass in brick of this nature.

[3] Robert B. Sosman, The Properties of Silica, p. 417. Chemical Catalog Co., New York, 1927.

With this information in view, it seems at least reasonable to assume, until further information is available, that the peculiar behavior of magnesite and recrystallized SiC brick, with respect to the variation of thermal conductivity with temperature, is likely due to their highly crystalline nature.

Apparently it requires only a small percentage of amorphous material to change the character of this variation completely as illustrated by the reversal in sign of the temperature coefficient when a small amount of ceramic bond is added to SiC crystals, corresponding to the Norton brick.

VI. Conclusions

The thermal conductivity of recrystallized and clay-bonded silicon carbide and fireclay and silica brick has been determined between 300°F and 2600°F.

The thermal conductivity of recrystallized SiC brick decreases with an increase of temperature in a similar fashion to the magnesite brick.

The clay-bonded SiC and fireclay and silica brick show an increase of thermal conductivity with an increase of temperature.

There is no evidence of the thermal conductivity of the brick varying with rate of heat flow or temperature gradient.

A possible explanation for the decrease of thermal conductivity with increase of temperature in the case of the recrystallized SiC and the magnesite brick has been suggested.

ROGERS LABORATORY OF PHYSICS
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

VITRIFIABLE COLORS FOR DECORATING GLASSWARE*

By W. E. Dougherty

ABSTRACT

The use of vitrifiable colors to be applied and fused on glassware is discussed. A brief history of the art is given, together with a discussion of the chemical composition and manufacture of the various types of colors.

I. Introduction

Vitrifiable colors, known best in the trade as glass colors, are applied and fused on to the surface of a finished piece of glassware. The history and use of this method has no relation to another type of decorated glassware, that is, where coloring compounds are introduced into the glass batch. This latter type is as old as glassmaking itself, as the first glass was probably colored by impurities in the raw materials used. The art of applying and firing vitrifiable colors on to glass, on the other hand, is comparatively new among the arts.

(1) Treatise by Theophilus on Glass Painting

The Chinese claim to have made glass 2000 years before the Christian era, and Egyptologists claim that glass beads in imitation of jewels were made in 4000 B.C., but there is no record of firing vitrifiable colors on glass until 1000 A.D. A monk, Theophilus, of the 10th Century has left a lengthy treatise on glass painting in which he describes the preparation of the color, manner of application, and the details of the firing process. For suitable brushes, Theophilus recommended the hair of the martin, ermine, or squirrel, and today the finest of the so-called camel's hair brushes are really made of squirrel hair.

The only color used seems to have been a purplish brown which was made up of iron rust, black copper oxide, and a so-called borax flux. These materials were ground thoroughly together on a glass or stone plate using a glass muller. The grinding medium recommended was wine.

The firing process was much the same as the present-day method of firing colors on window glass. The pieces of glass were bedded in silica, allowing only the painted surface to be exposed to the fire.

Theophilus' painting of glass was of the simplest nature, being only a tinting or shading of figures built up of pieces of colored glass which had been cut into definite shapes and afterward leaded together.

(2) Stained Glass Windows

During the period from the 10th to the 16th Century the art of stained glass windows reached a very high plane. Some of the work of this period is today recognized as examples of some of the most artistic work of mankind. These early glassmakers were well acquainted with the coloring properties of various elements and produced some remarkably fine yellow, blue, and ruby glasses, together with crystal and white. During the 16th Century, however, this industry began to decline and it was not until about 1850 that it was revived.

(3) Decorating Hollow Glassware

Glass decorating of the present-day style probably had its beginning about 1800 in Bohemia, which was then the center of the European glass industry. There are records which show that a Bohemian, Eckerman, was decorating glassware with vitrifiable colors at about that time.

With the discovery and development of oil as an illuminant, decorating of glassware came into vogue first on the lamp chimneys, well remembered by their red and yellow daisies and bands. When the more sumptuous parlor lamps, made of opal glass, came into use, artists of the highest type turned to decorating glass and produced remarkably fine effects in wild life, landscape, and floral designs. For the most part, the colors for this work were produced in Bohemia and other European glass centers where the results of continuous experimentation and development had been handed down from father to son.

With the continued demand for vitrifiable colors, the American importers, shortly after the beginning of the present century, began to duplicate the foreign-made materials and with the foreign supply almost entirely cut off by the world war an intensive research led to the production in this country of all types and shades of colors suitable for decorating glassware.

* Presented at the Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February, 1934 (Glass Division). Received February 15, 1934.

II. Vitrifiable Colors for Glass

(1) The Flux In developing vitrifiable materials for use on glass, the manufacturer is first confronted with the problem of putting together ingredients which, after being properly melted together and ground to a necessary fineness, will produce a material which will fuse thoroughly with a high gloss at a temperature considerably lower than the softening point of the glasses on which the color is to be fused. The color must have the proper coefficient of expansion so that it will not chip off or craze after the firing process has been completed, and it should not be readily attacked by the mild alkalis used in cleaning glassware. To meet these conditions it has been found necessary to use a relatively large amount of lead oxide in preparation of these colors, and the fluxing material has therefore become known in the trade as lead flux, although it has with it a considerable portion of boric acid, together with silica, feldspar, and other glass-forming materials. The ordinary flux contains approximately 65 to 75% PbO, 20% B_2O_3, and the remainder is silica, alumina, soda, potash, etc.

(2) Coloring Oxides While a few colors are made by melting simple coloring chemicals such as cobalt oxide or copper oxide into the flux, the majority are made by compounding with the flux coloring materials known as coloring oxides. In some instances, the coloring oxides are merely ground thoroughly with the already-melted flux, while in others the prepared coloring oxides are melted into the flux.

The coloring oxides are, for the most part, very complex compounds. The exact chemical compound responsible for the color of the material in some instances is not known. Their preparation consists briefly in mixing the raw materials intimately and calcining at relatively high temperatures. The calcining temperature is definite for each particular type of color and varies approximately from 2000 to 2700°F.

(3) Blues The essential element in all blue oxides is cobalt, as any one knows who is familiar with the use of cobalt oxides or other compounds in making blue glass. The tone of blue produced, however, when melting the oxide or a simple salt into a glass batch is a dark purplish one, and the glass color maker seldom resorts to this procedure of melting cobalt oxide into a flux. But if a cobalt-blue coloring oxide has first been developed by calcining cobalt oxide or a salt with alumina, silica, zinc oxide, or a mixture of these materials, a much cleaner and pleasing tone of blue results. When chromium oxide is introduced into the batch, still greener tones are obtained, yielding the so-called blue-green and turquoise shades.

(4) Chromium Greens For greens, chromium oxide itself produces an olive-green tone and is seldom used. However, when chromium compounds are calcined with calcium salts and silica, the result is a clean sparkling yellow-green which is used not only in glass colors but is used extensively in pottery industries as an underglaze color, where it is known as Victoria green.

A number of green shades used for decorating glass are made up of mixtures of yellows with blue-green or turquoise shades. Careful selection of both yellow and turquoise colors is necessary since, for example, should the yellow reflect too high a percentage of red, on being mixed with the turquoise color, the red and blue will produce theoretically black and the result will be a green having a dark or olive cast.

(5) Yellows Yellows are usually obtained with lead antimonates, cadmium sulfides, barium chromate, lead chromate, and uranium compounds.

(6) Brown and Black The brown oxides are prepared from iron chromates, together with manganese and nickel compounds. The blacks are made up of cobalt, manganese, and iron chromates.

(7) Reds The red colors fall into four distinct types: (*a*) those made from red iron oxide, (*b*) lead chromates, (*c*) gold, and (*d*) cadmium-selenium sulfides. The gold colors are important because the shades produced have not been duplicated with any other compounds. The gold is used in the form of purple of Cassius, and the red or ruby color is due to the gold being in a colloidal suspension. Weakened out they produce carmines, and pink tones. The addition of blue yields purples, violets, etc.

The red glass colors in which cadmium-selenium sulfide is used are a recent development and the method is interesting from the standpoint of the chemical reactions involved. Those who are familiar with the use of the lead compounds in connection with sulfides will appreciate the difficulty of combining in a glass both lead

and sulfur. These two elements react readily to produce the black lead sulfide, and it would seem that the fusion of these two elements into a glass batch would inevitably result in a color having at least a considerable proportion of black lead sulfide. Clean, brilliant red colors, however, have been obtained by mixing the cadmium-selenium sulfide red into a lead flux and having present another compound of cadmium which is soluble in the flux. The other cadmium compounds (for example, the oxide) may be present as an ingredient in the flux batch or it may be present by having been ground with the already prepared lead flux and the cadmium-selenium sulfide.

Any sulfur released from the cadmium-selenium sulfide during the firing operation will more readily combine with the cadmium oxide present to form the yellow cadmium sulfide than with the lead present to form a black lead sulfide.

(8) Transparent Colors Of the various colors manufactured, there are three types: transparent, opaque, and mat. The transparent colors are essentially lead borates into which has been melted a definite amount of coloring oxide which dissolves in the flux and acts as a stain. Obviously the coloring agent must dissolve completely in the flux during the melting process; otherwise the color would not be transparent when it has been applied and fired on to the glassware.

(9) Opaque Colors For the production of opaque colors and whites, the manufacturer must introduce into the lead flux an opacifying material which is insoluble or almost entirely insoluble in the flux. This has been accomplished by two distinct methods. By the first, opacity may be given the flux by introducing into the batch fluorine-containing compounds, such as cryolite or fluorspar. By the second method, insoluble opacifying materials, such as tin oxide, zirconium oxide, titanium oxide, or various molybdenum compounds, are ground thoroughly with the already-melted lead borate. Obviously this opacified lead flux may be colored by having coloring materials already melted into the lead flux or by grinding coloring oxides together with the flux and insoluble opacifying materials.

(10) Mat Colors Mat colors, so-called, because they have no gloss after being fired on the ware, were first introduced in France under the name "Gouache color." They are prepared by mixing or grinding with the lead flux a relatively large amount of material which does not dissolve in the flux on firing. There are quite a number of materials used for this purpose and they include zinc oxide, tin oxide, alumina, titanium oxide, magnesia, and clay.

These mat colors, of course, may also be tinted with the various coloring oxides and where a very intense color is desired there is sometimes added to the flux a sufficient amount of coloring oxide not only to produce the intense color but also to produce the mat effect.

III. Preparation of Glass Colors

For the preparation of glass color, the manufacturer selects the raw materials with the greatest care and uses chemicals of practically chemically pure quality. This is especially true with the chemicals used in making the various coloring oxides.

(1) Mixing The first step in the manufacture is mixing the raw batch. This is usually done by first brushing the raw materials through a fine-mesh screen and then mixing thoroughly the screened chemicals.

(2) Melting The melting of the batch is done in a small furnace much like an ordinary glass tank or may also be carried out in crucibles. Crucibles, however, are used only where a relatively small amount of a particular shade of colored glass is to be made, while the tank-like furnaces are used for making the large amounts of lead flux and opacified flux, where the opacifier is introduced into the glass batch. After melting, the glass is run into water to reduce the particle size as far as possible in preparation for the grinding process.

(3) Grinding To reduce the length of grinding time, the fritted glass or color is crushed to approximately 100-mesh before it is ground down to the proper fineness. During the early days of glass color manufacture, the colors were ground to fineness through a stone burr mill, like those used today in the manufacture of paint. Later, with the development of the pebble mills, these were used and are in general use at the present time. For the most part, glass colors are ground in water. Occasionally other grinding mediums, such as alcohol, acetone, or turpentine, are used in

order to prepare the color for certain definite requirements.

Since the methods of application of the color to the ware demand that the color be ground extremely fine, the grinding operation becomes a very important part of the manufacture and usually before a mill of color is emptied a fineness test is made. Since the color is ground much finer than would be retained on any screen, the fineness test is made by introducing some of the wet paste into a graduated cylinder, diluting with water and, after thorough shaking, allowing the color to settle out. Any coarse or unground particles will settle to the bottom of the cylinder much faster than the finer material and be readily detected.

After being properly ground, the wet color paste is dried and brushed through a fine screen to break up the cake obtained on drying.

IV. Production of Different Tones

In order to produce the thousands of different tones of colors, the manufacturer resorts to mixing the various basic colors, fluxes, and white enamels.

(1) Ivory In producing a definite shade of ivory, the color maker usually starts with a lead antimonate yellow, ground with a white enamel to weaken it out to the proper strength and then to this is usually added small amounts of other coloring oxides to bring the color over to the proper tone. It may be necessary to add a brown or a pink or a combination of the two. For this work a wide experience is necessary, first in analyzing the color to determine exactly what tones are necessary and then in determining the proper materials to add in order to produce this desired tone.

(2) Grays Grays are usually very difficult to match. At first it would seem that a simple mixture of white and black would produce a gray. A gray produced in this manner, however, is not at all pleasing to the eye and it is usually necessary to compound with the black and white other colors which may range from blue-green to pink, red, and brown. Even the black colors require compounding since in some cases a blue-black is more pleasing than a brownish or a greenish one.

In this compounding it is necessary for the color maker to know which colors can be mixed together with safety from the standpoint of chemical reactions which may occur when the compounded colors are fired on to the glassware. This is especially true with the pink, carmine, and ruby colors in which gold is used as the coloring agent.

V. Glass Ice Decoration

Another type of decorating material which is fused on to glassware is known to the glass decorator as "ice." The ices are small bead-like particles of white or colored glass which are produced by crushing the melted glass and sifting out the proper-sized grains. In composition they are similar to the ordinary flux and they are colored by introducing coloring elements or prepared coloring oxides into the glass batch.

VI. Stains

Aside from the vitrifiable colors, the glass decorator uses a number of other materials to produce various decorative effects. Among these is silver stain, sometimes called orange stain or amber stain. The discovery of this material was made during the 14th Century and it has been used extensively in church-window decorating as well as in the decoration of the ordinary glassware. In preparation of the stain, a silver salt, usually the chloride or the sulfide, is thoroughly ground with ocher and a paste of this mixture with water is applied and fired on to the glass. After firing, the coating is washed off with water. The reactions which produce the resulting amber stain are not definitely known. The stain, however, is perfectly durable in that it can not be removed by acids or alkalis and, in fact, is as permanent as the glass itself. High potash glasses are usually stained to a greater degree than the soda glasses, and tones ranging from the palest yellow to the deepest amber can be obtained by adjusting the silver content of the stain to suit the composition of the glass.

VII. Lusters

Another interesting type of decorative finish is that obtained with the so-called lusters. These are metal resinates, which are dissolved in essential oils and are applied to the glass in liquid form in the thinnest possible film. During the firing operation these metal resinates

decompose, leaving a thin film of metal or metal oxide on the ware. This coating in some cases produces a definite color and in other cases produces iridescent or mother-of-pearl effects. For example, where gold resinate is used the resulting color is pink or ruby, depending upon the thickness of the coating. Uranium produces yellow and the usual mother-of-pearl luster is a mixture of the resinates of tin, titanium, and bismuth.

VIII. Conclusion

The various decorating processes, such as banding, spraying, and printing have not been discussed; neither has the firing process by which the colors are fused into the glass been described. The application and firing of glass colors are an art and should be presented at another time.

O. Hommel Company
Pittsburgh, Pa.

BLISTERING AND CRAWLING OF GLAZES CAUSED BY UNDERSLIPS*

By H. G. Schurecht

ABSTRACT

Blistering of glazes during spraying and crawling during firing may be caused by the use of improper underslips. Blistering may be reduced by increasing the amount of clay in the underslip and reducing the more nonplastic ingredients. Crawling may be prevented by reducing the shrinkage and increasing the dry strength of the underslips.

I. Introduction

Blistering of glazes during spraying and crawling during firing may be caused by the use of improper underslips. With certain underslips, blisters $^1/_{16}$ to $^1/_8$ inch in diameter may develop on the surface of the glaze immediately after spraying (see Fig. 1). This tendency to blister becomes greater if too much time elapses between spraying the underslip and glaze. Crawling of the glaze may originate from shrinkage cracks in certain underslips (see Fig. 1). The purpose of this work was to determine some of the fundamental causes of these defects and methods of preventing them.

II. Experimental Methods

Twelve underslips whose compositions are given in Table II were studied. Two coats of underslip were applied to 4- by 4- by 1-inch dry terra cotta tile. After waiting ten minutes, the first coat of glaze was applied. Second and third coats were sprayed after five-minute intervals. The underslips and glaze were sprayed thicker than is normally done to accentuate the defects.

Shrinkage measurements of the underslips were made on 1- by $^1/_2$- by 4-inch bars molded of the same in the plastic condition. The absorptions of the raw bars were obtained by immersing these in kerosene for 48 hours while that of the fired bars was determined by boiling in water for five hours.

In calculating the ratio of clay to nonplastics, the free silica of the clay was figured as nonplastic as well as Cornwall stone, feldspar, fluorspar, flint, and whiting.

III. Results of Blistering Tests

It is apparent from the data given in Table II that this type of blistering is decreased as the amount of nonplastic is lowered. This defect probably originates from air in unfilled pores of the underslip which may develop shortly after spraying. Underslips which develop the largest amount of unfilled pores directly after spraying, would, therefore, develop the most blistering since in subsequent spraying the air in the unfilled pores is forced to the surface causing blisters.

It is evident, therefore, that an underslip which has a tendency to retain water throughout its pore structure will be less apt to cause blistering of the glaze. The ability of underslips to retain water is largely governed by its capillary attraction and permeability to water.

The capillary attraction of water may be represented by the following formula:

---

* Presented at the Annual Meeting, American Ceramic Society, Cincinnati, Ohio, February, 1934 (Terra Cotta Division). Received February 13, 1934.

$$H = \frac{2Y}{grd}$$

H = capillary height (cm.)
g = 981, gravitational acceleration (cm./sec.²)
r = radius of capillary tube
d = density of liquid at temperature of observation
Y = surface tension (dynes/cm.)

It is apparent from this formula that as the value, r, is increased the capillary attraction is decreased. By increasing the nonplastics in the underslip, the average value for r is increased and hence its capillary attraction and ability to retain water is decreased.

The writer[1] has previously shown that as the plasticity of clays is decreased their permeability to water is increased.

It is evident, therefore, that increasing the nonplastics in an underslip decreases both its capillary attraction and increases its permeability, tending to reduce its ability to retain water. This probably accounts for the fact that under-

TABLE I

RESULTS OF BLISTERING TESTS

Underslip	Appearance of glaze after spraying		
	First glaze coat	Second glaze coat	Third glaze coat
1	Slightly blistered	Badly blistered	Very badly blistered
2	O. K.	O. K.	Very slight blistering
3	O. K.	O. K.	O. K.
4	O. K.	Badly blistered	Very badly blistered
5	O. K.	Slightly blistered	Badly blistered
6	O. K.	O. K.	O. K.
7	Slightly blistered	Badly blistered	Very badly blistered
8	O. K.	O. K.	Slightly blistered
9	O. K.	Slightly blistered	Blistered
10	Blistered	Very badly blistered	Very badly blistered
11	Slightly blistered	Badly blistered	Very badly blistered
12	O. K.	O. K.	O. K.

TABLE II

COMPOSITIONS OF THE UNDERSLIPS

	1	2	3	4	5	6	7	8	9	10	11	12
Cornwall stone	44.5	19.9		45.0	45.0	41.0	30.0		49.5	35.0		
Potash feldspar		11.0	20.0					35.7			25.0	20.0
Fluorspar											5.0	4.0
Flint	9.9	4.4		10.0			30.0	19.0		35.0	30.0	
Whiting								7.0				
No. 9 Perrine clay		22.1	40.0		30.0							36.0
English china clay	24.8	33.2	40.0	25.0	25.0	35.1	20.0	19.0	27.5	15.0		40.0
English ball clay						23.4		19.0			20.0	
Kentucky ball clay	19.8	8.9		20.0			20.0		22.0	15.0	20.0	
Soda ash	1.0	0.5				0.5		0.3				
Borax									1.0			

TABLE III

PROPERTIES OF UNDERSLIPS

No. of underslip	Ratio of clay to nonplastic	Resistance to blistering	Resistance to crawling	Shrinkage			Absorption of raw underslip (%)	Absorption of fired underslip (%)
				Drying (%)	Firing (%)	Total (%)		
3	1.50	Excellent	Very poor	6.6	7.2	13.8	18.8	7.83
6	1.41	Excellent	Good	8.1	6.8	14.9	13.9	0.40
12	1.38	Excellent	Very poor	7.0	6.3	13.3	18.0	9.03
2	1.14	Very good	Fair	5.8	7.0	12.8	16.1	4.40
9	0.98	Good	Fair	5.9	8.5	14.4	18.1	5.28
4	0.82	Fair	Excellent				17.7	5.10
1	0.81	Poor	Excellent	5.7	6.2	11.9	16.2	4.80
5	0.67	Fair	Excellent	5.0	6.5	11.5	16.3	6.13
11	0.67	Poor	Poor	6.1	5.7	11.8	17.2	8.55
7	0.67	Poor	Excellent	5.0	7.0	12.0	15.9	6.60
8	0.61	Good	Fair	6.2			13.4	7.63
10	0.43	Very poor	Poor	5.0	6.8	11.8	15.7	6.93

[1] H. G. Schurecht, "The Mechanical Movement of Water through Certain Clays and Its Control," *Jour. Amer. Ceram. Soc.*, **5** [12], 935-36 (1922).

slips high in nonplastics cause more blistering than those low in nonplastics.

Underslip 8 seems to be an exception to this rule since it has a low ratio of plastics to non-

Underslip 3 | Underslip 6 | Underslip 1

FIG. 1.—Glazed samples showing crawling, blistering, and no defects when the same glaze was applied on different underslips. The same glaze applied on underslip 3 caused crawling, on underslip 1 it caused blistering, while on underslip 6 it remained free from defects.

plastics, but still has good resistance to blistering. Whiting, however, is more plastic and finer grained than the other nonplastics which probably accounts for this exception.

IV. Results of Crawling Tests

It is evident from Table III, that underslips having the greatest resistance to crawling should have a low shrinkage and high dry strength. For example, underslips 3 and 6 both have high shrinkage, but 6 is fairly strong with good resistance to crawling, while underslip 3 is weak and hence easily cracked in drying causing crawling. Underslip 10 has a low shrinkage, but still developed considerable crawling probably due to its low dry tensile strength. Underslips with low shrinkage and high dry strength, like underslip 1, usually possess excellent resistance to crawling.

V. Summary and Conclusion

Investigations to determine the causes and methods of preventing blistering and crawling indicate that these defects may be reduced by the following methods:

(1) Blistering of glazes during spraying may be reduced by reducing the amount of nonplastic ingredients in the underslip and increasing the clay content.

(2) Crawling of glazes caused by underslips may be prevented by reducing the shrinkage and increasing the dry strength of the underslips.

THE EASTERN TERRA COTTA COMPANY
LONG ISLAND CITY, N. Y.

CERAMIC ABSTRACTS[1]

Compiled by the

AMERICAN CERAMIC SOCIETY

Ross C. Purdy, Editor

Abstracters: A. Ally, J. B. Austin, A. A. Ayars, R. Barta, M. H. Berns, L. T. Brownmiller, W. M. Cohn, J. L. Gallup, Max Hartenheim, F. G. Heck, R. A. Heindl, E. B. Hewitt, G. M. Hutt, S. Kondo, M. V. Kondoidy, A. Kuechler, J. T. Littleton, A. J. Metzger, S. I. Perkal, J. G. Phillips, R. H. H. Pierce, Jr., W. E. Rice, G. R. Shelton, H. H. Stephenson, H. Türk, E. J. Vachuska, H. F. Vieweg.

Vol. 13 **June, 1934** **No. 6**

Abrasives

Properties of abrasive polishes. Alfred B. Searle. *Soap*, **10** [1], 23–25 (1934); abstracted in *Metal Cleaning & Finishing*, **6** [3], 133 (1934).—There are usually four stages in polishing: (1) grinding, (2) abrading with either a wet or dry abrasive, (3) abrading with the abrasive in a vehicle other than water, (4) polishing with a cloth or pad of soft material. Commercial polishes for repolishing metal contain essentially a detergent, an abrasive, a vehicle (which may also be a solvent), and color and perfume to increase the sales value of the product. E.J.V.

Cleaning polishing wheels. Fred B. Jacobs. *Metal Cleaning & Finishing*, **6** [3], 136–37 (1934). E.J.V.

Nature of polish layers. J. A. Darbyshire and K. R. Dixit. *Phil. Mag.*, **16** [108], 961–74 (1933).—The nature of the polished surface of a series of metals and a few other materials has been examined by means of electron diffraction patterns. The pattern of the high polished surface was found to be quite different from that of crystalline unpolished material. The polished layer appears to be an amorphous substance resembling a supercooled liquid. In the case of conductors the atomic volume of the surface layer appeared to correspond more nearly to the minimum values but in the case of selenium and silicon the normal interatomic distances are observed. J.T.L.

Cracks, heat-treatment, and grinding. M. Biscavart. *Aciers spéciaux*, **7** [8], 298–308 (1932).—The tendency of some steels to develop cracks in heat treatment, particularly under grinding, is discussed. To prevent the latter the following recommendations are made: Alundum 38 is preferred on account of its physical and structural properties; the binding material should maintain the grains in good, sharp condition. The grinding machine should have an arrangement to lift it off the piece to be ground when the grinder ceases to press against it; the grinder should be instructed to avoid working the grinding wheel too long on the same spot because of local heating; softer grades of abrasives are better, and dry grinding is preferable to wet grinding. Examples are given. M.H.

Producing expanding arbors. Fred B. Jacobs. *Abrasive Ind.*, **15** [3], 10–11 (1934).—Arbors in some form are among the most essential of machine-shop tools. J. describes the grinding operations on sleeve and taper body of an expanding arbor to provide rapid, accurate production. Illustrated. A.J.M.

Taper shank end mill grinding. Fred B. Jacobs. *Abrasive Ind.*, **15** [4], 14–15 (1934).—J. describes the production of end mills and gives drawings showing the setup of grinding wheels used. A.J.M.

Centerless grinding methods. A. D. Meals. *Abrasive Ind.*, **15** [3], 14–15 (1934).—A detailed description of the operations on flanged bushings and straight and flared valve stems is given. Illustrated. A.J.M.

Finishing connecting rod bores. John E. Kline. *Abrasive Ind.*, **15** [4], 13 (1934).—A method of honing connecting rod crankpin bores developed by the Hutto Engineering Co. is described. A.J.M.

Removing burrs from reamers. John E. Hyler. *Abrasive Ind.*, **15** [4], 25 (1934).—H. describes and illustrates an easily constructed fixture for holding reamers while burrs are removed. A.J.M.

Grinding rods to close tolerances. Cincinnati Grinders, Inc. *Abrasive Ind.*, **15** [4], 12 (1934).—Illustrated. A.J.M.

Motors and control equipment. R. E. W. Harrison. *Abrasive Ind.*, **15** [4], 10–11 (1934).—A general description of types of motors adaptable to grinding machines is given. A.J.M.

Grinding pistons and liners. Edwin Bremer. *Abrasive Ind.*, **15** [4], 8–9 (1934).—Abrasive operations used by the Dall Mfg. Co. are described. Illustrated. A.J.M.

Grinding small air compressor parts. Dayton Air Compressor Co. *Abrasive Ind.*, **15** [3], 13 (1934).—Illustrated. A.J.M.

Disk grinding coil spring ends. Gardner Machine Co. *Abrasive Ind.*, **15** [3], 12 (1934).—Illustrated. A.J.M.

Evolution of the abrasive industry. M. Biscavart. *Aciers spéciaux*, **7** [6], 231–35 (1932).—The importance of abrasives in metal working and the processes and materials used are discussed. M.H.

[1] The bold-face number following the journal is the volume, the issue number is in brackets, followed by the page numbers, then the year in parentheses.

Cleveland Tractor Co. grinds many parts. EDWIN BREMER. *Abrasive Ind.*, **15** [3], 8–9 (1934). Illustrated. A.J.M.

BOOKLET

Technical aspect of polishing grain. NORTON CO. Reviewed in *Foundry*, **62** [1], 62 (1934).—The topics discussed include the functioning of polishing grain, abrasive developments, bonding strength, grain-shape influences, controlled sizing of grains, and factors of efficient polishing. F.G.H.

PATENTS

Grinding the treads of wheel rims for rail vehicles, etc. EWALD HANUS. U. S. 1,951,977, March 20, 1934.

Abrasive apparatus. J. J. WALSH (Stratmore Co.). U. S. 1,952,003, March 20, 1934.

Brake-shoe grinder. R. E. W. HARRISON AND F. S. HAAS (Cincinnati Grinders, Inc.). U. S. 1,952,130, March 27, 1934.

Grinding machinery. J. E. CASTER, F. J. THELER, AND G. N. BARRERE (Cincinnati Grinders, Inc.). U. S. 1,952,157, March 27, 1934.

Grinding machine. B. R. PURVIN (Cincinnati Grinders, Inc.). U. S. 1,952,182, March 27, 1934. A. H. DALL AND HANS ERNST (Cincinnati Grinders, Inc.). U. S. 1,952,423, March 27, 1934, and U. S. 1,954,442, April 10, 1934. F. S. HAAS (Cincinnati Grinders, Inc.). U. S. 1,952,432, March 27, 1934. F. P. BROWN (Brown and Sharpe Mfg. Co.). U. S. 1,952,653, March 27, 1934.

Device for grinding bottoms of circular chasers. W. J. HOGG (National Acme Co.). U. S. 1,952,206, March 27, 1934.

Device for grinding pilot holes in circular chasers. W. J. HOGG (National Acme Co.). U. S. 1,952,207, March 27, 1934.

Machine for sharpening saw blades. J. L. LITOMY. U. S. 1,952,323, March 27, 1934.

Automatic grinding and polishing machine. W. V. ROBINSON. U. S. 1,952,334, March 27, 1934.

Abrading machine. D. C. PAGE (Heald Machine Co.). U. S. 1,952,458, March 27, 1934.

Vacuum attachment for cylinder hones. K. W. CONNOR AND F. M. KERN (Micromatic Hone Corp.). U. S. 1,952,492, March 27, 1934.

Buffing machine. W. M. SPRY (Peerless Machinery Co.). U. S. 1,952,634, March 27, 1934.

Polisher with reservoir. A. G. DECKER (Black & Decker Mfg. Co.). U. S. 1,952,910, March 27, 1934.

Construction of grinders for use in lathes, etc. EMIL RITZ, JR. (Hisey-Wolf Machine Co.). U. S. 1,953,133, April 3, 1934.

Grinding wheel construction. E. J. LINTEREUR. U. S. 1,953,181, April 3, 1934.

Refacing tool for flush valve seats. W. D. WILLARD U. S. 1,953,284, April 3, 1934.

Manufacture of rubber-bonded abrasive articles. H. C. MARTIN (Carborundum Co.). U. S. 1,953,984, April 10, 1934. The process of making rubber-bonded abrasive articles comprises preparing a viscous, mushy, semisolid yet stirrable mass of liquid and rubber so distributed therein as to thicken the mass sufficiently to hold the abrasive material in suspension during the mixing and forming of the article, mixing granular abrasive material with such mass, forming the articles from the mixture in a mold, drying the articles at pressures less than atmospheric, and subjecting the dried articles to pressures sufficient to consolidate the rubber and abrasive grain.

Machine for abrading concrete surfaces. JOE WILKS. U. S. 1,954,111, April 10, 1934.

Polishing or buffing wheel. D. H. ROSS AND L. J. NOOK. U. S. 1,954,263, April 10, 1934.

Grinding wheel. S. H. SCHURR (Lees-Bradner Co.). U. S. 1,954,330, April 10, 1934.

Grinding wheel mounting. ARCHIBALD CUNNINGHAM. U. S. 1,954,560, April 10, 1934.

Grinding device. GEORGE PEARSON. U. S. 1,954,575, April 10, 1934. A device for dressing breaker points is described.

Built-up abrasive element. H. R. STRATFORD (Stratmore Co.). U. S. 1,954,655, April 10, 1934.

Truing apparatus. EDWARD SOBOLEWSKI (Cincinnati Grinders, Inc.). U. S. 1,954,771, April 10, 1934.

Grinder. A. F. HOWE. U. S. 1,955,129, April 17, 1934.

Wheel dressing mechanism. C. L. OTT, E. P. WINE, AND H. E. BALSIGER (Landis Tool Co.). U. S. 1,955,202, April 17, 1934.

Lapping tool. C. W. FLOSS. U. S. 1,955,362, April 17, 1934.

Abrasive papers and cloths. Z. HADNAGY AND A. M. BOUILLARD. Brit. 406,581, March 7, 1934.

Multiple-purpose machine for sawing, filing, grinding, slotting, etc. A. H. EVANS AND C. N. FLETCHER. Brit. 406,681, March 14, 1934.

Grinding or abrading tools for extremely hard alloys. P. VOGELI-JAGGI AND DIAMANT-SCHLEIFEREI VOEGLI & WIRZ AKT.-GES. Brit. 406,921, March 14, 1934.

Valve-seat grinding tools. G. W. JOHNSON (Hall Mfg. Co.). Brit. 407,186, March 21, 1934.

Precision grinding machines. A. SCRIVENER. Brit. 407,209, March 21, 1934.

Glass polishing tools. PILKINGTON BROS., LTD., AND F. B. WALDRON. Brit. 407,406, March 28, 1934.

Glass-grinding apparatus. PILKINGTON BROS., LTD., AND F. B. WALDRON. Brit. 407,407, March 28, 1934.

Device for grinding poppet valves. C. ALLEN. Brit. 407,481, March 28, 1934.

Abrading or finishing slots, keyways, splines, etc., in metal parts. C. TALBOT, LTD., AND F. W. TRENDELL. Brit. 407,742, April 5, 1934.

Abrasive-coated materials. W. J. TENNANT (Behr-Manning Corp.). Brit. 407,978, April 11, 1934.

Machine for grinding, polishing, and marking razor blades. H. BASSAT. Brit. 408,012, April 11, 1934.

Machine for grinding pins, rollers, tubes, etc. H. A. DUDGEON. Brit. 408,037, April 11, 1934.

Method and device for machining razor blades. E. SIEPMANN & CO. Brit. 408,118, April 11, 1934.

Art and Archeology

Chemistry and art. C. G. FINK. *Ind. Eng. Chem.*, **26** [2], 234–38 (1934).—An artistically decorated, unglazed Greek vase of the Brooklyn Museum was saved from the corrosive action of sodium, magnesium, aluminum, and calcium salts which covered the surface of the vase. Examination showed that some of these salt crystals had lifted the pigment particles away from the original surface of the vase. If the surface had been washed with water and a soft brush, these pigment particles would have been lost. Accordingly, electroösmosis was adopted by using the porous vase as a semipermeable partition and placing a cathode wire inside the vase and an anode wire outside, near the decoration. After electrolyzing for a short time, the salt crystals disappeared and the little pigment particles were forced back into place. After carefully drawing off the water outside the vase while the current was still on and allowing the vase to dry, it was sprayed with a lacquer to anchor the pigment particles permanently on to the surface of the vase. Illustrated. F.G.H.

Chemicals for glass etching. WILLY HACKER. *Diamant*, **56** [6], 66 (1934).—Several compositions used for etching glass and their application are briefly described. M.V.K.

C. I. E. colorimetric standards and their use. T. SMITH AND J. GUILD. *Trans. Opt. Soc.*, **33**, 73 (1931–32).—The new international standards, which define a standard observer, three standard illuminants, standard conditions of illuminating and viewing opaque specimens, a standard for evaluating the brightness factor of opaque specimens, and a standard trichromatic system for the expression of color measurements, are stated and their origins are explained. J.T.L.

Decoration by impression in two fusions. MARCEL BERTHON. *Céram., Verrerie, Email.*, No. 4, pp. 201–202 (1933).—By decorating on green dried ware instead of on biscuit ware one fusion is eliminated. Details of the method are given. M.H.B.

Defects and their removal in metal porcelain. F. DOBROVSKY. *Keram. Rund.*, **41** [49], 647–48 (1934).—The copper deposit must be as thin as possible and without pores. The second galvanic layer usually consists of nickel which often dulls after a certain time, due to the presence of bath crystals in the pores. Chromium porcelain has a better resistance. Discolorations or the destruction of the nickel chromium layer is due to faulty treatment when fired. The porosity of the metal layers is avoided by keeping the baths clean and by continually controlling their composition. The defects in silver porcelain are due to the oxidation of silver in the air and are removed by covering it with a transparent lacquer. M.V.K.

Use of suede as pottery finish. ROBINSON-RANSBOTTOM POTTERIES. *Ceram. Ind.*, **22** [4], 185 (1934).—"Suede pottery" pieces are turned as with ordinary pottery but instead of glaze, suede, the same material used on expensive shoes, is applied with a high-pressure air brush. The new finish resists water and comes in mulberry, green, blue, and yellow. E.J.V.

Contemporary design and the problem of the ceramic shop. CARLTON ATHERTON. *Design*, **35** [7], 9–10 (1934).—The element of fine design has been unnecessarily submerged in learning the manipulation of the machine because its difference is only in size and speed. To produce poor design with such a tool means stultification of the entire process. The manufacturer, merchant, and salesman share the blame for the tawdry ornate ceramic articles shown. They approve perfection of technique but neglect or ridicule the principles of design, sacrificing the art quality possible through output of time and money devoted to perfection of design to economic pressure for immediate returns. The ceramic shop needs a ceramic designer with a conception of (1) quality of body and glazes for specific uses, (2) basic form suited to purpose and practical manufacture, and (3) surface ornament, if any, to replace the imported designer unaware of the American pattern of life. E.B.H.

Courage ⇄ Revolution ⇄ Color. MATTHEW LUCKIESH. *Enamelist*, **11** [6], 13 (1934).—L. points out how the courage born of dissatisfaction with the old order leads to revolution, which in turn leads to new life and color. Color is more prominently associated with courage than with weakness. Colors may be warm, cool, neutral, stimulating, depressing, tranquil, striking, weak, harmonious, gaudy, quiet, subdued. L. points out that more color should be used in homes, theaters, stores, etc. E.J.V.

B.A.I.D. sculpture competition. ANON *Pencil Points*, **15** [3], 147 (1934).—Two prize-winning vases from the competition at the Beaux Arts Institute of Design are shown. One vase was designed to hold small trees or flowering plants with a possibility of planting vines on the side, and its setting among furniture, etc., was to influence its color ornament. E.B.H.

Art in industry: two exhibitions. ANON. *Art*, **27** [2], 96–97 (1934).—The Museum of Modern Art opened an exhibition in March, and the National Alliance of Art and Industry sponsored one at Rockefeller Center opened February 15. Both showed industrial art emphasizing the victory of machine art over the handicrafts. E.B.H.

"Couverte" on the windows of Chartres Cathedral. ANON. *Jour. Brit. Soc. Glass-Painters*, **5**, 35–36 (1933–34). (*J.S.G.T.*)

Art glass reaches new heights. F. E. MAYER. *Amer. Glass Rev.*, **53** [23], 19–20 (1934).—Windows for the "Cathedral of the Air" are described. A.J.M.

Seasons in domestic glass. E. A. KENT. *Jour. Brit. Soc. Glass-Painters*, **5**, 19–24 (1933–34).—The subjects of the months and seasons are frequently found in ancient glass, both domestic and ecclesiastical. References are made to some roundels in which these subjects occurred. Illustrated. (*J.S.G.T.*)

Zachariah Boreman. WILLIAM H. TAPP. *Connoisseur*, **93** [389], 28–36 (1934).—Zachariah Boreman was called the father of landscape painting on china. T. describes his work. Illustrated. E.B.H.

Spanish and American folk art. HESTER JONES. *Design*, **35** [9], 8–12 (1934).—J. gives a brief history of the pottery of Spanish and Indian origin and illustrates some typical pieces. E.B.H.

National factory of Bing and Grøndahl porcelain.

ANON. *Danish Foreign Office Jour., Commercial Rev.*, **13**, 175–78 (1933).—Ten illustrations of new *genres*, dull porcelain and enamel glazes, are given. H.H.S.

Old Derby china. G. B. HUGHES. *Christian Sci. Mon.*, **26** [111], 5 (1934).—The celebrated Derby porcelain manufacture began in the Derby Pot Works on Cockpit Hill about 1746, when André Planché designed simple white figures of animals and modeled them in pastes of his own composition. In 1756 William Duesbury became connected with the works and was succeeded by his son, William, in 1786. The third generation of Duesburys leased the works to Robert Bloor who made cheap and gaudy materials. The reputation of the ware suffered and in 1845 the works were closed. In 1796 a harder paste was used, with a greenish translucency and a thinner uncrazed surface which did not absorb the paint, but from 1815, when Bloor took control, there was a lack of transparency in the somewhat heavy paste and the glaze had a tendency to crack and cause discoloration. Derby is famous for its modeled figures, both decorated and in the biscuit, the latter being unglazed white figures resembling alabaster. Various marks on Derby china are explained and the work of the different modelers and painters is discussed. Illustrated. E.J.V.

The de Pass pottery in the Fitzwilliam Museum. BERNARD RACKHAM. *Connoisseur*, **93** [392], 245–48 (1934).—This Museum at the University of Cambridge has one of the leading public collections of pottery in England. The de Pass group includes (1) a late 14th Century majolica bowl of Persian form with the cross-hatched background typical of early ware and copper green over an enamel whose grayish white tone is due to the small proportion of tin; (2) a jug with graffito decoration from northern Italy differing from true majolica in having not an opaque tin glaze or enamel but a transparent lead, usually yellowish, over a coating of white slip through which the design is scratched disclosing the buff body; (3) and (4) plates of Urbino ware painted by the famous Xanto, showing only slightly the transparent washes of one pigment over another conspicuous in his later work and minus the manganese purple; (5) a later Urbino dish, the under side painted to simulate the sky with flying figures, although the subject was usually the sea with swimming creatures; (6) two specimens of Valencian lustered ware (Hispano-Moresque); (7) a dish of Bernard Palissy and a tile from a stove showing similar techniques done in different countries, England and Germany, contemporaneously. Illustrated. E.B.H.

Heraldic glass in London. F. SYDNEY EDEN. *Connoisseur*, **93** [392], 249–55 (1934).—E. describes and illustrates examples of heraldic glass still existing in two churches in London. E.B.H.

Development of drinking glasses. C. F. GREEVES-CARPENTER. *Glass Ind.*, **15** [3], 30–31 (1934).—The development of drinking glasses is traced from the neolithic age when earthenware and bronze utensils were being produced, through the use of wooden tankards, drinking horns, pewter mugs, leather drinking vessels, to drinking glasses made in the 17th Century and since. Types of drinking glasses made in the European countries are described. Illustrated. E.J.V.

Samian ware made in Roman Britain. M. R. HULL. *Illus. London News*, **184**, 96–97 (1934); see following abstract. H.H.S.

Romano-British pottery at Colchester. ANON. *Nature*, **132** [3337], 598 (1933).—Further details of finds of Roman potters' kilns at Colchester are given. Eight kilns were discovered. Four of these widely spaced, had been used for jugs, mortars, and other vessels in coarse buff ware. The second four, concentrated in a small area and surrounded by a retaining wall, were buried 5 to 8 ft. beneath material containing many fragments of Samian molds and ware. This was evidently the place where Samian ware was produced. Old style British and Samian mass production articles were found side by side. Stamps on Samian ware were well-known names of potters whose factories are known in eastern Gaul and Germany. These marks also appear on color-coated Castor ware decorated with hunting scenes and also made at Colchester. The stamps and similarities of form and mold, linking the ware with examples of known date from the Continent, together with the finding of a coin of Marcus Aurelius fix the date at about A.D. 180 to 200. *Ibid.*, **132** [3346], 542 (1933).—Excavation at Colchester in 1933 has yielded the names of two potters inscribed on the Samian (terra sigillata) ware. Examples of their work have previously been discovered both at Colchester and at Veralumin. Indications point toward finding evidence to prove the existence of a local factory, thus confirming the view that Samian ware was made in Great Britain as well as imported. Stamps on Terra Sigillata, by Felix Oswald (*Ceram. Abs.*, **11** [3], 153 (1932)) are indispensable in studying Samian ware. Examples not listed in this work, but all by previously known potters, may be found in a Catalogue of Potter's Stamps on Terra Sigillata found in Gloucester, by Charles Green (Public Museum, Gloucester, Occasional Papers No. 1, Price 6d). In all there are 56 specimens, dating from Nero to Antonine. Pre-Flavian and Flavian stamps are all of south Gaulish potters. Thirty-nine come from central Gaul and three are from eastern Gaul. See also *ibid.*, **13** [3], 52 (1934). J.L.G.

The art of the German folk. EDWIN REDSLOB. *Design*, **35** [9], 3–7 (1934).—From native clay the potter turns jugs and plates which are decorated by pouring liquid color from a can like an oil can. Birds of clay are decorated with ornament adjusted to the material. E.B.H.

Examples of French enamel painting. BESSIE BENNETT. *Bull. Art Inst. Chicago;* reprinted in *Enamelist*, **11** [6], 21 (1934).—The technique of painting in enamels on smooth, flat copper developed in Limoges, France, in the latter half of the 15th Century. Small but exceedingly precious objects of art were produced in the early 16th Century, when the process reached the point of perfection. Nardon Pénicaud, the founder of a dynasty of artists, was the most illustrious of the old enamelers. A description of his "Flagellation, Crucifixion, and Descent from the Cross," a triptych on exhibition in the section of Ecclesiastica of the Art Institute in Chicago, is given. None of his successors equaled the craftsmanship and the splendor of coloring he achieved with a translucent glazing over a ground of intense white. A small coffer enameled by him is also described. Illustrated. E.J.V.

Pottery of Milan and Lodi. TERNI DE GREGORY.

Connoisseur, 93 [391], 158–62 (1934).—In the 18th Century a vogue for Chinese ware brought to Europe through the East India Co., quantities of porcelain services and ornaments from the Orient. Accurate majolica imitations of Chinese ware were made at the factories of Felice Clerici and of Pasquale Rubati (formerly with Clerici) at Milan and by Ferreti at Lodi. Many of these pieces have been cherished for two centuries as Chinese. Typical Rubati ware has flowers and insects in low relief in pale colors outlined in gold. Delftware was also reproduced. Genuine pieces of these majolicas can be distinguished from the modern imitations by their lightness and by a soft grayish bloom on the enamel which is seemingly impossible to reproduce. Illustrated. E.B.H.

An Oriental hunting bowl. H. A. Bryden. *Connoisseur*, 93 [392], 256–57 (1934).—A fine old Oriental punch bowl done by Chinese copyists is remarkable because the various hunting scenes, taken from English designs, are well depicted and easily identified. Illustrated. E.B.H.

History of Egyptian pottery. Anon. *Pottery Gaz.*, 59 [682], 473–74 (1934).—The first pottery of Egypt proper is Tasian, about 5000 B.C., hand made, probably coil built, with a smooth but rather uneven surface. The color was a mixture of brown and black due to insufficient knowledge of firing. In the predynastic period, about 4000 B.C., stoneware was produced from a different clay fired to a much higher temperature. Decoration of the ware was also begun. At about 3000 B.C. the hand wheel made its appearance, to be followed by the true potter's wheel in 2800 B.C. (Fourth Dynasty). The art of making fine pottery then slumped with occasional revivals in 2000 B.C., 1500 B.C., and 400 A.D., but with no permanent effect. Glaze on faience was introduced early in Egyptian history, but the true glazed pottery did not make its appearance until the Arab period. The types of ware produced at different times are discussed. Illustrated. E.J.V.

International notes: discoveries. E. M. Benson. *Art*, 27 [3], 140 (1934).—The beauty of the mosaics recently discovered near Beirut, Syria, seems to excel the great animal art of the Scythians. The floor of only one villa of this buried city remains, but its mosaics represent animals in characteristic movements. Illustrated. E.B.H.

PATENTS

Design for glass bottle. D. S. Anderson (Scotia Distillers, Ltd.). U. S. 91,750, March 20, 1934.

Design for bottle. C. M. Plochman (Plochman & Harrison). U. S. 91,787, March 20, 1934. W. J. Latchford, Jr. (Bohemian Distributing Co., Ltd.). U. S. 91,829, March 27, 1934. L. S. Rosenstiel (Schenley Products Co., Inc.). U. S. 91,843, March 27, 1934. Alfred Schneier (Advance Pressure Castings, Inc). U. S. 91,846, March 27, 1934. E. W. Fuerst (Owens-Illinois Glass Co.). U. S. 91,867, April 3, 1934.

Design for lighting fixture bowl. Nicholas Kopp (Kopp Glass, Inc.). U. S. 91,781, March 20, 1934.

Design for wall bracket. R. G. Cowan (Pass & Seymour, Inc.). U. S. 91,860, April 3, 1934.

Design for coffee pitcher. A. F. Fukal (Chicago Flexible Shaft Co.). U. S. 91,868, April 3, 1934.

Design for coffee maker. A. F. Fukal (Chicago Flexible Shaft Co.). U. S. 91,869, April 3, 1934.

Design for tile. W. W. Kellogg. U. S. 91,883 to 91,885, April 3, 1934.

Design for plate. A. E. Mayer (Mayer China Co.). U. S. 91,892, April 3, 1934. Alfred Duhrssen. U. S. 91,924, April 10, 1934.

Design for glass bowl. George Sakier (Fostoria Glass Co.). U. S. 91,909, April 3, 1934.

Design for sharpening stone. S. G. Blake (Carborundum Co.). U. S. 91,979, April 17, 1934.

Design for jar. Gwynne Evans (David G. Evans Coffee Co.). U. S. 91,993, April 17, 1934.

Design for wall-bracket lamp. Edward Kanter. U. S. 92,004 to 92,006, April 17, 1934.

Design for combined teakettle and cover. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,032, April 17, 1934.

Design for combined saucepan and cover. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,033, April 17, 1934.

Design for combined sauce pot and cover. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,034, April 17, 1934.

Design for combined sauce kettle and cover. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,035, April 17, 1934.

Design for combined double boiler and cover. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,036, April 17, 1934.

Design for cover for pot, pan, kettle, etc. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,037, April 17, 1934.

Design for saucepan. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,038, April 17, 1934.

Design for sauce pot. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,039, April 17, 1934.

Design for drip coffee pot. Alexis de Sakhnoffsky (Vollrath Co.). U. S. 92,040, April 17, 1934.

Process for the decoration of ceramic ware. E. C. Guisinger. U. S. 1,951,868, March 20, 1934.

Material for decorating surfaces. A. H. Ernst (E. I. du Pont de Nemours & Co.). U. S. 1,954,353, April 10, 1934. A composition, on firing at a temperature of below about 770°C, produces a substantially white adherent nonscumming palladium-gold alloy decorative deposit on ceramic surfaces comprising a solution of palladium and gold in an organic liquid in such quantities that the ratio of palladium metal to gold is between the limits of about equal quantities and ten times as much gold as palladium.

Producing gold leaf decoration on glass by transfer process. J. Koutnik. Ger. 569,281, Jan. 12, 1933. By printing, lithographic, etc., processes, the decoration or letters are produced on transfer paper in imitation gold and are assembled on adhesive paper, being applied by means of colored gelatine to the glass plate which is backed with real gold leaf. The adhesive paper and transfer paper being removed, the real gold leaf is cleaned off by means of turpentine from between the decoration which is, of course, protected by the imitation leaf, and the whole is then backed by means of colored varnish. (*J.S.G.T.*)

Cements

Chemical resistance of cements. C. VITTORI. *Ingegnere*, No. 2, pp. 92–95 (1933); abstracted in *Bibliografia Italiana* [Series C], **6** [9–10], 80 (1933).—The chemical resistance of various cements was tested by immersion in solutions of magnesium, calcium, copper, and ammonium sulfate, calcium chloride, tannic acid, various organic substances, and distilled water. H.F.V.

Notes on cement manufacture. I–II. A. M. *Verre & Silicates Ind.*, **5** [1], 11–13; [3], 48–49 (1934).—A brief account of the firing of cement and of furnaces used is given. M.V.K.

PATENT

Process of manufacturing cementitious materials. A. J. BLANK (Cement Process Corp.). U. S. 1,953,924, April 10, 1934. The process of producing a cementitious product comprises mixing a calcareous material containing lime in a form reactive to silica and alumina with a material selected from the group consisting of silica sands, siliceous earths and clays, and other argillaceous and argillo-calcareous materials generally known to be suitable as the raw materials for supplying the siliceous and aluminous components in Portland cement manufacture and previously reduced to a fineness of approximately 90% through a 200-mesh screen or finer, the mixing being carried on in the presence of an amount of water sufficient to insure hydration of any quicklime present and sufficient to insure the presence of free moisture in the mixture throughout the mixing operation, and in the presence of an accelerating agent and while mixing, maintaining the mixture at a temperature of at least 100°C and not exceeding about 400°C, to produce mutual reactions between the lime and the siliceous components of the material.

Enamels

Control of raw materials. II. Determination of alkalis in feldspar. ANON. *Amer. Enameler*, **6** [10], 3–4 (1934).—The method used in determining the alkalis in feldspar is described in detail. **III.** *Ibid.*, **7** [1], 4 (1934).—The determination of the various properties of feldspar such as calcium carbonate, calcium fluoride, silica, magnesium oxide, etc., is described. See also *Ceram. Abs.*, **13** [4], 81 (1934). H.T.

Feldspar: how it is found and prepared. J. P. ROGERS. *Amer. Enameler*, **6** [10], 5–6 (1934).—The method employed in locating the proper feldspar and the geographical location of feldspar veins are described. H.T.

Saltpeter as enamel raw material. ANON. *Glashütte*, **63** [46], 820–21 (1933).—The chief value of saltpeter is as an oxidizing, refining, and decolorizing medium. It is seldom used in enamel in any form, be it potash, soda, or nitrate. The action of potassium nitrate or soda saltpeter in the enamel fusion is essentially the same. Barium nitrate can be used only for majolica and powder enamels and then only as an oxidizing agent. M.V.K.

Barium nitrate as enamel raw material. ANON. *Glashütte*, **63** [42], 696 (1933).—Experiments showed that it is advantageous to replace saltpeter by barium nitrate in frits and generally to use it as a fluxing agent, especially for enamels containing lead. M.V.K.

Notes on vitreous enamels and colors. A. ENGLAND. *Sheet Metal Ind.*, **8** [82], 125–26 (1934); abstracted in *Metal Cleaning & Finishing*, **6** [3], 134 (1934).—Three essentials must be considered in building up an enamel formula: (1) the melting temperature of the finished enamel, (2) the expansion of enamel, which must closely approximate that of the enamel on which it is applied, and (3) the elasticity of the enamel, which must not chip. Steel for enameling purposes has a cubical coefficient of expansion of 0.00004 and an enamel to fit this must have an expansion of approximately 0.00003. A clear cover enamel formula of proper expansion is given. Decreasing the percentage of silica and alumina will lower the melting temperature of the enamel, but this varies the coefficient of expansion and a mathematical problem is introduced. The lower the modulus of elasticity, the more easily the enamel is stretched. Typical Young's modulus values for enamel constituents are given. In the production of colored enamels cobalt oxide is probably the one most used. It enters into the composition of blues, blacks, and certain greens. E.J.V.

Ceramic color oxides and opacifiers. GEORGE A. LEE. *Can. Chem. Met.*, **18** [3], 52 (1934).—L. enumerates some of the commonly used oxides for obtaining opacity and various shades of color and explains the rigidly controlled methods used in matching color samples. E.J.V.

Progress in the field of acid-resisting enamels. D. B. WALTERS. *Better Enameling*, **5** [3], 8–9 (1934); *Can. Chem. Met.*, **18** [3], 53 (1934).—In spite of many efforts to improve acid-resisting enamels it has been impossible to get results comparable to those obtained with ordinary finish-coat enamels. Because of the difficulties associated with the application of acid-resisting enamels they have not been used for many purposes to which they could logically be adapted. The ideal acid-resisting enamel should have good covering power with the addition of 4% tin oxide and should match the ordinary enamels in color and luster. It should also mature under approximately the same heat treatment as ordinary enamel, should require no special set-up agents, and should retain its set and working properties over a considerable length of time. Frits capable of meeting these specifications are now available, and they appear likely to achieve the same classification of workability and results as the nonacid-resisting cover coats. The acid-resisting enamels have possibilities of increasing the use of porcelain enamel products. E.J.V.

Adherence of sheet-iron ground enamel. H. SCHAARSCHUH. *Glashütte*, **63** [48], 811–19 (1933).—The hammer scale present on the sheet iron prevents adherence of the enamel; it is completely dissolved by the enamel. The scale checks the surface stresses which cause a uniform coating of the iron surface by the enamel. The adherence of cobalt and nickel ground enamel on sheet iron is a chemical process, a conversion of the metallic iron into

silicate. The dissolving of the metallic iron is not uniform; it dissolves more along the grain edges. The dissolving rate of separate iron crystals varies. The dissolving of the iron out of the sheet iron is conditioned by the capacity of the cobalt silicate to dissolve iron. At the same time, a partial splintering of iron particles takes place during dissolving. These iron particles cause a reduction of Co^{III} by the metallic Fe, and an exchange of iron and cobalt occurs in the silicate. Illustrated.
M.V.K.

Manufacture of enameled shields and posters. HEINRICH SASSE. *Glashütte*, **63** [42], 693–95; [44], 727–29; [46], 776–80; [47], 794–96; [49], 836–38 (1933).—S. discusses in detail (1) the preparation of the raw ware, (2) the properties of sheet iron, (3) contrivances employed, (4) shaping of shields, (5) pickling baths, (6) calcining of the raw ware, (7) preparation of the enamel and its fusion, and (8) enameling of the ware. M.V.K.

Cast-iron enameling and the effect of good foundry practice. H. G. WOLFRAM. *Can. Chem. Met.*, **18** [3], 61–62 (1934).—A study of the blistering of enamels during application to cast iron has led to the conclusion that a hard surface layer or microchill is the cause of blisters. This microchill is thought to be cementite or combined carbon which breaks down under the enameling temperature to finely divided "temper carbon"; this in time oxidizes, forming CO and CO_2, which cause blisters in escaping through the enamel. The effect of "burned in" sand, phosphorus, sulfur, and manganese in cast irons is discussed. A new charging technique was developed for producing quality cast iron, and a better casting analysis is set up as standard. E.J.V.

What should be the constitution of cast iron for enameling? GUSTAV KREBS. *Emailwaren-Ind.*, **10** [17], 135–36 (1933).—To obtain good results in enameling, the cast iron must be carefully prepared. It must contain at least 0.8% P, which, although it makes the iron brittle, lowers its solidification point and its tendency to absorb C during melting. Si dissolves coal, converts it into graphite and precipitates the coal surplus as "kish." Mn combines with C. It increases the capacity for absorbing carbon and CO. Cast iron should contain 3.4% C, 2.5 Si, 0.6 Mn, 0.8 to 0.9 P, and 0.08 to 0.1 S. The proper casting temperature is from 1380 to 1400°. The process of casting is discussed. M.V.K.

Blast cleaning in the metal industry. WILLIAM A. ROSENBERGER. *Machinery*, **40** [6], 353–56 (1934); abstracted in *Metal Cleaning & Finishing*, **6** [3], 132 (1934). E.J.V.

Oxyacetylene welding for porcelain enamel. L. B. HART. *Enamelist*, **11** [6], 9 (1934).—When welding for porcelain enamel there are four sources of trouble: materials, design and forming, welding equipment, and welders. Materials suitable for welding and enameling should be free from segregated impurities and gas-forming materials. It has been found advisable in designing a product where welds must be made to so design it that the greater portion of the weld consists of base metal alone, whether it is a butt weld or a lap weld. Properly designed jigs, clamps, etc., are also important. Welding torches should be kept clean and free from the accumulation of oxides that splash and stick to the tip. For porcelain enamel all welded seams should be formed with a neutral flame. Welders should be trained not to sacrifice quality for quantity and should be thoroughly schooled in welding for porcelain enamel.
E.J.V.

Capacity of various opacifiers in enamels and glazes. F. H. ZSCHACKE AND G. VITALI. Presented at International Ceramic Congress at Milan, 1933; abstracted in *Glashütte*, **63** [47], 794 (1933); *Sprechsaal*, **66** [52], 887–88 (1933).—Three enamels were used, the first being a "normal" composed of 58.7% SiO_2, 29.0 PbO, 10.0 K_2O, 2.0 Na_2O, and 0.3 As_2O_3. In the second series of the boric acid variety, 4.5% SiO_2 was replaced by B_2O_3; in the third series of the alumina variety, 4.5% SiO_2 was replaced by Al_2O_3. To these ground enamels increasing quantities of opacifier were added. It was determined that 4% As_2O_3 produces a complete opacification in enamels free from boric acid and alumina, while in the alumina variety, 2% As_2O_3 deeply opacifies the enamel. The behavior of fluorides, zircon dioxide, antimony compounds, tin compounds, phosphates, etc., was determined. Experiments with phosphates in combination with calcium showed that tricalcium phosphate does not opacify sufficiently. Two groups of glazes with a normal borate glaze, baryta, and lead glaze with opacifiers similar to those used for enamels were investigated. The glazes were fused with the opacifiers, the degree of opacification was determined, and the powdered glazes were fired on bodies. The behavior of the various opacifiers differed greatly. It was found that from a practical viewpoint glazes containing baryta are throughout similar to glazes containing lead.
M.V.K.

Installation and operation of pickling installations in enamel works. RICHARD ALDINGER. *Keram. Rund.*, **41** [45], 598–601 (1933).—Illustrated. M.V.K.

Notes on enameling. X. A. H. *Verre & Silicates Ind.*, **5** [3], 49–51 (1934).—A discussion of the pickling, washing, neutralizing, and sandblasting of the raw ware is given. For Parts VIII–IX see *Ceram. Abs.*, **13** [4], 81 (1934). M.V.K.

Thermal economy in enamel works. E. WIEDEMANN. *Glashütte*, **63** [38], 628–31; [41], 676–79; [43], 709–11; [45], 742–44 (1933).—W. discusses in detail thermal losses occurring in enamel kilns such as (1) loss of fuel through the grate, (2) heat losses through kiln walls, (3) losses due to cooling of the muffle when opening the muffle door during charging and discharging, and (4) loss of waste gases. Means of lowering the losses applied in different types of kilns are discussed. Illustrated.
M.V.K.

Application of statistical methods in practical cupola furnace operation. K. NEUSTAETTER. *Giesserei*, **21** [7–8], 71–74 (1934).—Statistical methods are eminently suitable for investigating conditions in rough operations such as in foundries, etc. An example of a cupola furnace operation illustrates how conditions and factors which are not at once obvious in their influence can be related to the general operation. M.H.

Hand or electrically operated powder table for enameling bathtubs. OSCAR KERSTAN. *Glashütte*, **63** [39], 653–54; [40], 665–66 (1933).—The principles of operating the table and its advantages are discussed. Illustrated. M.V.K.

Latest developments in enameling. II. EMERSON P.

POSTE. *Ceram. Ind.*, **22** [4], 201–206 (1934).—P. continues his review of the literature covering enamel processing, firing enamels, enamel equipment, and new uses for enamel. The future of the enameling industry depends on fundamental research. A white ground coat must be developed, and a softer acid-resisting enamel is desired. A better knowledge of materials is necessary and a wider application of enameled products is to be looked for. The building industry holds many possibilities for expansion in the use of enameled sheet steel. A greater adoption of the continuous enameling process is also to be sought. For Part I see *Ceram. Abs.*, **13** [5], 111 (1934). E.J.V.

Enamel shop troubles. R. ATKINSON. *Can. Chem. Met.*, **18** [3], 53 (1934).—These vary in cause from small amounts of soda ash, carried over from the neutralizer tank to the enameling process, to defects in the metal to which the coat is applied. In one case where blistering developed in the enamel on a fresh lot of metal which was pickled for ten minutes in the usual manner the microscope revealed that this was due to a difference in the steel used. Both types of steel pitted, but in the case where the enamel failed the pits were not clean to the bottom and a longer pickling remedied the trouble. Temperature and moisture content of the atmosphere in enamel furnaces frequently prove the solution of the enamel problems. E.J.V.

Enamel. III. W. MAVOR. *Clay Prod. News*, **7** [3], 6–7 (1934); for Parts I–II see *Ceram. Abs.*, **13** [3], 56 (1934). A.J.M.

Enamels. I. W. K. *Verre & Silicates Ind.*, **5** [4], 62–63 (1934).—A general discussion of enamels and their relationship to ceramics and the iron industries and a definition of enamels are given. M.V.K.

Application of black edge. DAVID HOY. *Enamelist*, **11** [6], 12 (1934).—A satisfactory method for the spraying of black edges on the unfired ground coat is described in detail. E.J.V.

Porcelain enamel as a building material. ANON. *Amer. Enameler*, **7** [1], 4–5 (1934).—The possibilities offered the dairy industry by this material, the progress of porcelain enamel in the industry, and its value from the standpoint of sanitation and cleanliness are discussed. H.T.

Ferro offices show new enamel uses. ANON. *Enamelist*, **11** [6], 22–24 (1934).—At the entrance is a porcelain enameled check, the trade-mark. Hand railings of white porcelain enameled pipe enclose the steps and the corridor is lined in ivory enameled sheets, secured to the walls by means of narrow aluminum strips. Eight large porcelain enameled murals, beautifully designed and executed by H. Edward Winter, decorate the main lobby. In the president's office are found another larger mural, a desk top covered with porcelain enameled steel tile, and a porcelain enameled coffee-table. The restaurant is also equipped with porcelain enameled tables, etc. Illustrated. E.J.V.

Story of the stove. NORMAN BEL GEDDES. *Fortune; Enamelist*, **11** [6], 16–18 (1934).—Illustrated. E.J.V.

Glorifying the gas pumps. H. DANA CHASE. *Better Enameling*, **5** [3], 10–12 (1934).—A discussion of the increasing use of porcelain enamel for gas-station exteriors and for the finish on gas pumps is presented. The advantage of this type of construction is pointed out. Illustrated. E.J.V.

PATENTS

Process of preparing vitreous enamel slips. R. M. KING (National Aluminate Corp.). U. S. 1,953,760, April 3, 1934. In the process of enhancing the setting-up properties of vitreous enamel slips the step of adding thereto a small amount of sodium aluminate is described.

Glaze or enamel. K. E. LONG (Harshaw Chemical Co.). U. S. 1,954,390, April 10, 1934. A composition of matter for glaze or enamel use comprises an available reactive base and antimony in ratio at least equivalent to that in antimonate, titania, and enough of such base to combine with the titanium.

Method of making enameled radiators. R. W. LOEFFLER. U. S. 1,954,638, April 10, 1934.

Enameling apparatus. W. W. GALBREATH AND R. M. CHESNEY (Youngstown Pressed Steel Co.). U. S. 1,955,491, April 17, 1934.

Glass

Application of Stokes' law in the determination of the absolute viscosity of glass. R. G. HUNTER. *Jour. Amer. Ceram. Soc.*, **17** [5], 121–27 (1934).

Preparation of sintered Pyrex brand glass filters. P. L. KIRK, R. CRAIG, AND R. S. ROSENFELS. *Ind. Eng. Chem., Anal. Ed.*, **6** [2], 154–55 (1934).—The preparation of sintered Pyrex brand glass filters from various particle sizes of glass to meet definite porosity specifications is described in detail. F.G.H.

Thermal expansion of soda-lime-silica glasses. E. SEDDON, F. WINKS, AND W. E. S. TURNER. Presented at meeting of Society of Glass Technology, Sheffield, Feb., 1934; *Pottery Gaz.*, **59** [681], 344 (1934) (by title). E.J.V.

Study of volatilization from lithium oxide-containing glasses. E. PRESTON AND W. E. S. TURNER. Presented at meeting of Society of Glass Technology, Sheffield, Feb., 1934; *Pottery Gaz.*, **59** [681], 344 (1934) (by title). E.J.V.

Investigation of glass types according to chemico-physical formulas and suggestion for an international classification. JOSÉ A. DE ARTIGAS. Presented at International Ceramic Congress, Milan, 1933; *Sprechsaal*, **66** [52], 886 (1933); *Glashütte*, **63** [49], 834 (1933). M.V.K.

Calculations of glass batch from glass analysis. III. J. A. MARTZ. *Nat. Glass Budget*, **49** [48], 7 (1934).—M. explains how to calculate the batch required to produce a glass of given chemical analysis. A list of "glass-to-batch" factors is given. **IV.** *Ibid.*, **49** [49], 10 (1934).—Examples of the use of the factors in calculating a batch are

given. For Parts I–II see *Ceram. Abs.*, **13** [3], 57 (1934). A.J.M.

New researches on the chemical stability of glass. G. KEPPELER. Presented at the International Ceramic Congress at Milan, 1933; abstracted in *Glashütte*, **63** [49], 834 (1933); *Sprechsaal*, **66** [52], 886–87 (1933).—Injuries to the stability of glass caused by chemical attack are due to the fact that important ingredients of the glass are soluble in water. Hence, almost all methods for judging the chemical stability of glasses depend on the determination of the rate with which these materials are dissolved by water, acid, and solutions of alkali. These investigations are made on the surface of the glass object; glass grit of a definite granulation is used when dealing with small quantities of glass. This method is chiefly used to study the influence of separate oxides and the effect of the variations in composition on the stability with similar kinds of oxides. The difficulties of using the results of such researches in practice are discussed. K. found that the temporary course of the attack is a parabolic function in which the perimeter for the liability to decomposition of the glass surface concerned is a characteristic quantity. The actual course deviates more or less from this regularity. The practical application of this law is discussed and illustrated by examples. M.V.K.

Significance of analysis for determining the flow of glass. A. THÜRMER. *Glashütte*, **63** [46], 768–70 (1933).—The migration velocity of separate oxides varies; hence, the homogenizing of the glass depends on the diffusion capacity of the glass components. When altering the batch, the effects on the change of flow should be considered. Slowly diffusing oxides should be varied in smaller amounts than those diffusing rapidly in order that the obstruction of the flow will not cause a concentration and lowering of the homogeneity of the glass. The change in the glass composition has no significance as to the proper thermal glass flow. Illustrated. Bibliography. M.V.K.

Physical testing of glass. M. CONTI. *Ind. Vetro e Ceram.*, No. 1, pp. 26–29; No. 2, pp. 55–59; No. 5, pp. 202–205; No. 6, pp. 230–34; No. 7, pp. 294–98; abstracted in *Bibliografia Italiana* [Series C], **6** [11–12], 47 (1933).—C. discusses the importance of tests and apparatus based essentially on the principles of physics and their application to the glass and ceramics industry. Particular attention is given to measurement of the thermal coefficient of expansion. Physical tests for homogeneity and the study of relation between chemical and physical-optical characteristics are discussed. H.F.V.

Glass for protection from infra-red radiation. E. H. HOBBIE. *Trans. Illum. Eng. Soc.*, **28**, 658 (1933).—A blue-green tinted glass, Coolite, is described and said to have the property of absorbing the infra-red and transmitting a large portion of the visible spectrum. Photometric curves are given out to about 3 microns showing the percentage of solar energy transmitted for the different wave-lengths. Three grades of glass, differing in their transmission values, are described. Data are given showing the temperatures attained in boxes covered with various glasses and exposed to sunlight. J.T.L.

Principals for testing hydrolysis of the glass surface. H. JEBSEN-MARWEDEL. *Sprechsaal*, **67** [1], 2–3 (1934); *Verre & Silicates Ind.*, **5** [3], 45–47 (1934).—Three important points exist when testing the surface hydrolysis of every kind of glass. An exact knowledge of the chemical behavior of the glass surface can be obtained only when these points are precisely established. Diagrams and formulas illustrate the discussion. M.V.K.

Intermediate region between the thermal and dielectric breakdowns. P. H. MOON AND A. S. NORCOSS. *Arch. Elektrotech.*, **27** [12], 827–31 (1933).—The thermal and electrical breakdowns of glass were investigated. The results are in a good agreement with former investigations. It is proved definitely that an intermediate region exists between the thermal and dielectric breakdowns. W.M.C.

Emission of ions from glass and rock crystal (transparent quartz) containers under the influence of radium rays. A. FERNAU. *Physik. Z.*, **34** [24], 899–900 (1933).—Irradiating conductivity water by means of β and γ rays will result in an increase of the conductivity. The increase depends on the material of the containers. It is assumed that under the influence of irradiation ions are liberated from the container walls. This is true even for containers made from the best transparent quartz obtainable. W.M.C.

Dependence of electrical conductivity of glass on tension. E. G. BÄCKER. *Z. Elektrochem.*, **39** [7*b*], 554–55 (1933).—The tension in hard glass can be determined from the electrical conductivity. E.J.V.

Water-salt balance in glassworkers. J. MATUSSEVITCH AND E. PEREGUD. *Zentr. Gewerbehyg. Unfallverhüt.*, **20** [1], 1–5 (1933); abstracted in *Chim. & ind.*, **30** [2], 319 (1933).—Observations made on sixty-eight glassworkers in Germany are discussed in detail. M.V.K.

Experimental study of the elastic characteristics of tempered glass. A. BRUSCHI. *Ricerche di Ing.* [Rome], **3**, 73–79 (1933); abstracted in *Bibliografia Italiana* [Series C], **6** [11–12], 104 (1933).—The relationship between deformation and stress was determined by compression tests on tempered glass and confirmed by photoelastic examination of flexed specimens. H.F.V.

Suggestions for the desirable requirements of stability for several kinds of glass. R. SCHMIDT AND F. SPÄTE. *Fachausschussber. Deut. Glastech. Ges.*, No. 26, pp. 55–62 (1933).—Suggestions for standardizing glass include sheet glass, hollow glass, bottle glass, medicinal bottle glass, luxury (crystal and artistic) glass, apparatus glass, pipe glass, illuminating glass, and optical glass. A literature index is given. M.V.K.

Cements and adhesives for safety glass. F. OHL. *Pottery Gaz.*, **59** [681], 350 (1934).—The transparent organic intermediate layer in about 90% of the safety glass is celluloid, 4 to 6% acetyl cellulose, and the rest from a number of materials, gelatin, artificial resins, etc. The thickness of the adhesive layer varies from 0.01 to 0.02 mm. up to 0.03 mm. for thin layers. With polymerides and artificial materials as adhesives, thicker layers from 0.05 to 0.1 mm. and over are used. These adhesives must (1) possess extremely good sticking power and durability when in contact with glass and the outer layers, (2) be stable to light, (3) be resistant to moisture and temperature alteration from −10 to 50°C and various weathering influences so that the adhesive power is not lost under changing conditions, (4) not react with the glass or the center

layer, (5) be easily applied and dry quickly, uniformly, and smoothly, and (6) possess elasticity. E.J.V.

Statistical investigation of the uniformity of grades of 1000 Lovibond red glasses. GERALDINE K. WALKER. *Bur. Stand. Jour. Research*, **12** [3], 269–82 (1934); R. P. 653.—The data show that variations of a whole unit frequently exist among glasses of similar Lovibond numeral. R.A.H.

Two-color glasses. LUDWIG SPRINGER. *Sprechsaal*, **67** [6], 78–79 (1934).—Different colors appearing in various layers of glasses can be promoted by using glass coloring oxides, especially nickel, cobalt, chromium, and uranium, which are little sensitive to oxidation or reduction and which are previously combined with such coloring materials as selenium. With lime crystal glasses beautiful two-color glasses may be produced, especially with uranium oxide and selenium. Under certain conditions, the intimate mixing of both glass colorizers does not produce a new color, but both colors remain independent. This is possible because the elementary glass pigments, *e.g.*, selenium, are present in a different state (only colloidally dissolved). M.V.K.

Constitution and color of chromium glasses. W. WEYL AND E. THÜMEN. *Sprechsaal*, **66** [12], 197–99 (1933); abstracted in *Chem. Zentr.*, **i**, 2992 (1933).—The green color of technical chromium glasses is due partly to bluish-green Cr^{III} compounds and partly to yellow Cr^{VI} compounds. The spectrum of such glass fused under O_2 at 200 atmospheres is analogous to that of an aqueous K_2CrO_4 solution. Pure Cr^{III} glasses are obtained by fusion under reducing conditions by addition of As_2O_3 or the use of glass free from alkali, *e.g.*, HPO_3. The effect of alkalis on the oxidation equilibrium of chromium glasses is discussed. Addition of B_2O_3 deepens the color. Soda borosilicate glasses melted under O_2 at 250 atmospheres have a yellow-brown coloring. They probably contain the hexavalent chromium in the form of a "hetero-poly acid" of B_2O_3 and CrO_3 molecules. M.V.K.

Notes on the manufacture of colorless glasses. No. 15. Devitrification. ANON. *Glass*, **10** [5], 184–88 (1933).—The important influences on devitrification are described under the following heads: (*a*) amount of silica present in the glass, (*b*) nature and proportion of fluxing oxide present, and (*c*) nature and proportion of stabilizing oxide present. A brief method of identifying the crystals formed on devitrification is given. **No. 16.** *Ibid.*, **10** [6], 228–33 (1933).—A further description of the means of identifying crystals formed on devitrification is given. The optical properties of crystals are briefly set forth and the use of the polarizing microscope is described. The optical properties of crystals which might be formed in soda-lime glasses are given. **No. 25. Thermal endurance.** *Ibid.*, **11** [3], 96–99 (1934).—The properties of glass affecting thermal endurance may be classified as thermal properties (thermal expansion, thermal conductivity, and specific heat) and mechanical properties (density, tensile strength, crushing strength, elasticity, and hardness). These properties are explained in detail. For No. 24 see *Ceram. Abs.*, **13** [5], 113 (1934). A.J.M.

Preparation of glass wool. SCHOOP. *Pottery Gaz.*, **59** [681], 315 (1934).—A possible new method for the preparation of glass wool is by use of an electrically heated metal spray gun which the molten glass leaves in the form of a large number of fine fibers of uniform diameter. E.J.V.

Use of proper glass to diminish glare of automobile lamps. A. MONNIER AND M. MOUTON. *Compt. rend.*, **196** [22], 1659–60 (1933).—Total elimination of blue and violet rays by a yellow glass with a Cd base has proved to increase visibility over white light by about 10% due to the lesser diffusion, even in foggy atmosphere, and greater sharpness of vision. Glare is entirely eliminated, and the normal vision of the eye, which requires 40 seconds for readaptation in white light, is restored in the yellow light after 4 seconds. M.H.

Apparatus for studying the birefringence of industrial glasses. J. ESCHER-DESRIVIÈRES. *Rev. d'Optique*, **11**, 215–21 (1932). (*J.S.G.T.*)

Decrease in the transparency of old window glasses for ultra-violet rays. H. VALENTIN. *Pharm. Zentr.*, **74**, 5–8 (1933); *Brit. Chem. Abs.*, **B**, p. 147 (1933).—Of a number of samples of window glasses tested, all showed a greater absorption of ultra-violet radiation after three years' illumination, while only one specimen showed any transparency for wave-lengths below 3000 Å after this period. (*J.S.G.T.*)

New standardization of sheet glass. BEIER. *Diamant*, **54**, 349 (1932).—Mechanical methods of sheet-glass manufacture have resulted in the substitution of two grades for the four qualities of handmade glass. The former first, second, and third qualities are included in the new grade 1, while the old fourth quality is now denoted as grade 2. Basic selling prices and the question of standardization of sizes of sheets have not yet been fixed. (*J.S.G.T.*)

What is implied by the term "full crystal?" ANON. *Glass Rev.*, **10** [2], 17–18 (1934).—"Full lead crystal," as applied to tableware, is defined by W. E. S. Turner as a glass containing not less than 30% by weight of lead oxide (PbO) and in which the alkali is in the form of potash, or if the soda is present at all, it is not in greater amount than 1.0%. A.A.

Essentials of glass technology based on American practice. VII. S. R. SCHOLES. *Ceram. Ind.*, **22** [4], 208–12 (1934).—Under the different types of furnaces, S. discusses pot, regenerative, recuperative, and plate-glass furnaces, the tank furnace, and day, continuous, and bridge-wall tanks. Illustrated. For Part VI see *Ceram. Abs.*, **13** [4], 86 (1934). E.J.V.

Cleaning glass containers. VIOLET DIMBLEBY. *Glass Rev.*, **10** [1], 14–16; [2], 26–28 (1934).—The solutions most commonly used as cleansing media are caustic soda and soda ash. Sodium metasilicate and trisodium phosphate are also used, frequently accompanying one or both of the stronger alkalis. An effective cleanser (*Glass Packer*, **12**, 435 (1933)) should have power to wet the glass surface and to deflocculate the dirt and should have emulsifying, dissolving, and germicidal power. The four chemicals mentioned above possess these powers in varying degrees. To remove the washing material a soft water should be used, as alkali on the glass surface will precipitate the salts in hard water forming a white deposit on the container. Chlorine may be added to the rinsing water when necessary to ensure sterility of the glass surface. A.A.

What are striae? ANON. *Glashütte*, **63** [35], 592 (1933).—A case of the appearance of striae on the surface of white hollow glassware is described. The glass was melted in an open "neck-tank" furnace. M.V.K.

What are streaks? A. M. *Glashütte*, **63** [35], 589–91 (1933).—M. discusses the term "streaks" and their origin in glass. M.V.K.

New machine for surfacing lenses. COLONEL CH. D'EVÉ. *Rev. d'Optique*, **10**, 201–12 (1931). (*J.S.G.T.*)

Is the temperature control in cooling furnaces economically justified? ANON. *Glashütte*, **63** [41], 679–82; [43], 707–708 (1933).—The importance of measuring temperature in cooling furnaces for hollow glassware is pointed out. Data on different thermoelements are given. M.V.K.

Continuous glass tank design. WM. G. BERGMAN. *Ceram. Ind.*, **22** [4], 190–91 (1934).—B. suggests a new glass tank which will effect improvements by confining the batch, the glass in process of melting, and the finished homogeneous glass to definite channels and force it to follow a path of maximum length and time. Ten advantages of this design are presented with a sketch of the new type tank. E.J.V.

Development of "Amco" glassmelting furnaces. CL. TEICHMANN. *Glashütte*, **63** [38], 627–28; [39], 651–53 (1933).—A description of different types of "Amco" glassmelting furnaces and of their development is given. Illustrated. M.V.K.

Discussion of a glass furnace using naphtha as fuel. F. PLATANIA. *Calore*, **6**, 132–34 (1933); *Ind. Silicati*, **11** [9–10], 7–9 (1933); abstracted in *Bibliografia Italiana* [Series C], **6** [11–12], 105 (1933).—The construction of small glass furnaces using naphtha as fuel is considered from a thermal viewpoint. The criteria for the most efficient preheating of air are discussed. H.F.V.

Development of modern glass bottle-making machinery. F. G. PASOTTI. *Trans. Jun. Inst. Eng.*, **43**, 229–71 (1933).—P. gives a more or less chronological survey of the development of the Owens, Daubenspeck, Moorshead, O'Neill (feeder-fed type), Monish, and O'Neill vacuum machines and then deals in some detail with the Hillman machine. The Ferguson and Hartford I. S. Redfern machines and the Roirant "B" and "F" machines are briefly mentioned. Illustrated. (*J.S.G.T.*)

Thirty-five foot glass-lined tanks in one piece for beer storage. A. O. SMITH CORP. *Ceram. Ind.*, **22** [4], 189 (1934). Illustrated. E.J.V.

Glass industry of Norway and Sweden. ANON. *Glass Rev.*, **10** [1], 1–6 (1934).—There is a small but active glass industry in Norway, including domestic glassware, general illuminating glassware, drawn sheet glass, rolled figured glass, frosted glass, and bottles. The Swedish glass industry is much more extensive than that of Norway. No plate glass or chemical glassware is made in Sweden at the present time. A.A.

Glass industry of Scandinavia. W. E. S. TURNER. Presented at meeting of Society of Glass Technology, Sheffield, Feb., 1934; *Pottery Gaz.*, **59** [681], 344–47 (1934). E.J.V.

Building with glass. L. WILLIAMS. *Arch. Rev.*, **73**, 92–94 (1933). (*J.S.G.T.*)

Glass as wall decoration. M. I. BATTEN. *Arch. Rev.*, **73**, 91 (1933). (*J.S.G.T.*)

Moth-wing glass for spring tables. ANON. *Arts & Dec.*, **40** [6], 23 (1934).—Moth-wing glass, fragile and with milky flakes, is executed by Maurice Heaton in handmade plates, bowls, and trays in green, yellow, gray, black, white, and henna. Illustrated. E.B.H.

Curiosities of glass painting. J. A. KNOWLES. *Jour. Brit. Soc. Glass-Painters*, **5**, 27 (1934). (*J.S.G.T.*)

Progress of the glass industry in 1932. II. OSCAR KNAPP. *Glashütte*, **63** [47], 791–92 (1933).—A brief review is given of investigations dealing with (1) crystalline structure of some glasses, (2) rate of crystallization of devitrification products in potash-lead glasses, (3) volatility and steam pressure of soda-silica glasses, (4) the system lime–boric acid, (5) formation of barium silicates, (6) effect of boric acid on the devitrification of soda-lime glasses, (7) behavior of manganese-colored glasses toward reduction, (8) dependence of density and optical properties on the chemical composition, (9) specific gravity of glass in dependence on temperature, (10) tensile strength of glass, (11) dielectric constants of glasses and their relationship to chemical composition, (12) thermal shock and mechanical strength of machine-made bottles. For Part I see *Ceram. Abs.*, **13** [4], 86 (1934). M.V.K.

This year of glass. J. GLOAG. *Arch. Rev.*, **73**, 85 (1933). (*J.S.G.T.*)

Old English glass. No. 50. FRANCIS BUCKLEY. *Glass*, **11** [3], 100–101 (1934).—An account of the war tax on glass in 1695 is given. Illustrated. For No. 49 see *Ceram. Abs.*, **13** [5], 116 (1934). A.J.M.

Early history of glassmaking in London. J. L. ARCHER. *Pottery Gaz.*, **59** [682], 475–76 (1934).—The early history of glassmaking in and near London, when the manufacture was in the hands of Royal patentees, is sketched. Illustrated. E.J.V.

Travels of a glass merchant two hundred years ago. ANON. *Diamant*, **54**, 445–46 (1932). (*J.S.G.T.*)

Schools of glass painting in King's Lynn and Norwich in the Middle Ages. C. WOODFORDE. *Jour. Brit. Soc. Glass-Painters*, **5**, 4–18 (1933–34). (*J.S.G.T.*)

BOOK

Yearly report of the Wärmetechnische Beratungstelle der deutschen Glasindustrie for 1932. I. Description of the application and efficiency of electrodes for glass-melting. II. Test on a Globar furnace with six rods with water-cooled ends. The furnace had a capacity of 250 kg. and a consumption of 60 kw. and its dimensions were 1000 mm. long, 650 mm. high, and 800 mm. wide. The temperature was automatically regulated to within 5°. The furnace could be heated from room temperature to 1100° in 96 hours; the control up to 700° enabled this to be done safely. The first melting carried out was on a window glass (Fourcault) mixture, charged on in three lots of 25, 25, and 16 kg. of 1200 to 1260°, and the temperature was then raised to 1340°; 1 kg. glass required 1.58 kw. hr. The time taken to reach a state fit for working out was from 20 to 25% shorter than with a producer gas-fired furnace. (*J.S.G.T.*)

PATENTS

Lens for head lamps. R. N. FALGE (General Motors Corp.). U. S. 1,950,978, March 13, 1934.

Bifocal lens and method for making. F. E. DUCKWALL (Continental Optical Mfg. Co.). U. S. 1,951,506, March 20, 1934.

Method and apparatus for cooling glass articles. W. H. RISING (Corning Glass Works). U. S. 1,951,950, March 20, 1934.

Take-off roll for glass tubing and cane. L. N. POND (N. V. Mij. tot Beheer en Exploitatie van Octrooien). U. S. 1,951,993, March 20, 1934.

Lens-grinding machine. J. J. MCCABE (Bausch & Lomb Optical Co.). U. S. 1,952,212, March 27, 1934.

Lens-blocking device. H. W. HILL (American Optical Co.). U. S. 1,952,373, March 27, 1934.

Lens. E. D. TILLYER (American Optical Co.). U. S. 1,952,394, March 27, 1934. H. W. LEE (Kapella, Ltd.). U. S. 1,955,590 and 1,955,591, April 17, 1934.

Process for glass designing. A. D. NASH (Libbey Glass Mfg. Co.). U. S. 1,952,454, March 27, 1934. A process of designing a glass article comprises molding a semi-fluid glass blank so that its outer surface is formed with raised portions, moving the blank so formed over powdered glass of the desired mesh and color, reheating the blank, remolding the blank to form other projections on its outer surface, again moving the blank through powdered glass of desired mesh and color, and then blowing the blank to finished form.

Glassmaking machine. E. B. HUNTER. U. S. 1,952,593, March 27, 1934.

Leer feeder. E. E. MILNER (Ball Bros. Co.). U. S. 1,952,680, March 27, 1934.

Method and apparatus for making glass. VERGIL MULHOLLAND (Hartford-Empire Co.). U. S. 1,953,023, March 27, 1934.

Glass shears. W. R. STERRETT (Ball Bros. Co.). U. S. 1,953,030, March 27, 1934.

Shallow melting tank. P. G. WILLETTS (Hartford-Empire Co.). U. S. 1,953,034, March 27, 1934.

Method and apparatus for feeding batch mixtures to furnaces. ROBERT GOOD (Hazel-Atlas Glass Co.). U. S. 1,953,221, April 3, 1934.

Sheet-glass cooler and process of absorbing heat. J. L. DRAKE (Libbey-Owens-Ford Glass Co.). U. S. 1,953,341, April 3, 1934.

Process and apparatus for sealing laminated glass. FRANK FRASER (Libbey-Owens-Ford Glass Co.). U. S. 1,953,344, April 3, 1934.

Method and means for feeding raw material to glass-melting furnaces. T. C. MOORSHEAD (United Glass Bottle Manufacturers, Ltd.). U. S. 1,953,427, April 3, 1934.

Laminated glass and method of making. W. H. MOSS (Celanese Corp. of America). U. S. 1,953,971, April 10, 1934.

Composite glass and process of making. M. L. MACHT (Duplate Corp.). U. S. 1,954,055, April 10, 1934.

Apparatus for grooving laminated glass. J. G. OLIVER (Pittsburgh Plate Glass Co.). U. S. 1,954,057, April 10, 1934.

Double glazing. J. C. PARKINSON (Pittsburgh Plate Glass Co.). U. S. 1,954,058, April 10, 1934.

Device for grooving safety glass. C. E. SMITH (Duplate Corp.). U. S. 1,954,061, April 10, 1934.

Plate glass. FREDERICK GELSTHARP (Pittsburgh Plate Glass Co.). U. S. 1,954,077, April 10, 1934.

Fuse box of Pyrex brand glass. A. G. STEINMAYER (Line Material Co.). U. S. 1,954,186, April 10, 1934.

Method and apparatus for making glass yarn. OSCAR GOSSLER. U. S. 1,954,732, April 10, 1934.

Glass-grinding apparatus. C. E. HENDERSON (Libbey-Owens-Ford Glass Co.). U. S. 1,955,128, April 17, 1934.

Process and apparatus for annealing sheet glass. DANIEL ADAMS (Libbey-Owens-Ford Glass Co.). U. S. 1,955,163, April 17, 1934.

Method of controlling the composition of glass. H. H. BLAU (Macbeth-Evans Glass Co.). U. S. 1,955,451, April 17, 1934. A method of modifying the composition of glass in the fused state comprises melting a glass batch, fractionating the glass by passing a direct electric current through the melt as an electrolyte, regulating the potential of the current to alter the concentration of a particular oxide of the batch in one region of the melt primarily by migration of such constituent from one region of the melt toward another to thereby produce a fraction of desired composition, and withdrawing the fractionated region of desired composition.

Method and means for feeding raw material to glass-melting furnaces. UNITED GLASS BOTTLE MANUFACTURERS, LTD., AND T. C. MOORSHEAD. Brit. 406,577, March 7, 1934.

Plants for tempering glass. R. MEER. Brit. 406,606, March 7, 1934.

Method of drawing glass tubes. N. V. MIJ. TOT BEHEER EN EXPLOITATIE VAN OCTROOIEN. Brit. 406,623, March 7, 1934.

Nonbrittle sheets for safety glass and their manufacture. TRIPLEX (NORTHERN), LTD., L. J-B. FORBES, AND W. B. PRICE. Brit. 406,644, March 14, 1934.

Methods and apparatus for cutting glass. BRITISH THOMSON-HOUSTON CO., LTD. Brit. 408,181, April 11, 1934.

Apparatus for making sheets of glass. SOC. ANON. DES MANUFACTURES DES GLACES ET PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY ET CIREY. Fr. 41,791, April 13, 1933; addition to 699,275. (*C.A.*)

Device for cutting glass. J. KIRSCHFINK. Ger. 564,531, Nov. 3, 1932. (*J.S.G.T.*)

Multiple gathering iron for feeding several molds. FIRMA F. W. KUTZSCHER. Ger. 565,131, Nov. 10, 1932. The individual irons are mounted on a common handle in such a way that they can be moved concentrically about a common axis for the purpose of adjusting their separation. (*J.S.G.T.*)

Preventing inrush of atmospheric air to parison mold of suction machines. EUROPÄISCHER VERBÄND DER FLASCHENFABRIKEN G. M. B. H. Ger. 565,759, Nov. 24, 1932. The plunger and neck ring operate in a chamber formed between the parison mold and a flange member on the plunger rod by a cylinder collar, and vacuum or pressure can be applied at will to this chamber. (*J.S.G.T.*)

Tunnel leers. T. TEISEN. Ger. 565,788, Nov. 24, 1932.

The waste gases are led on their way to the chimney through flues below the leer in order to warm up the return side of the belt. (*J.S.G.T.*)

Relieving rolls in vertical drawing shafts. K. KÜNZEL. Ger. 565,913, Nov. 24, 1932. Means are provided for raising one set of rolls from the others to permit the passage of irregular portions of glass such as those caused by stones. A signal device can be incorporated and the raising of the rolls can be carried out automatically. (*J.S.G.T.*)

Locking neck and parison molds together. EUROPÄISCHER VERBÄND DER FLASCHENFABRIKEN G. M. B. H. Ger. 566,543, Dec. 8, 1932. The parison mold halves are carried in frames which swing on arms about a common axis in such a way that the action of swinging together to close the mold wedges it up tightly against the neck mold. (*J.S.G.T.*)

Automatic machine for making light-walled glassware. EMPIRE MACHINE CO. Ger. 566,672, Dec. 8, 1932. A multi-arm machine of the press and blow type for making light-walled ware such as electric lamp bulbs is referred to. (*J.S.G.T.*)

Construction of leers and tunnel kilns. N. V. MIJ. TOT BEHEER EN EXPLOITATIE VAN OCTROOIEN. Ger. 566,717, Dec. 8, 1932. In leers provided with roller conveyers with the journaling and driving members located outside the leer, the walls are so constructed that the crown can move with the minimum friction over the walls bearing it. (*J.S.G.T.*)

Production of decorated glassware. SENDLINGER OPTISCHE GLASWERKE G.M.B.H. Ger. 566,965, Dec. 8, 1932. One or more layers of clear or colored glass are placed in the fluid state over a base glass and are pressed down by profiled plungers to give a pattern which is then polished or cut and polished. (*J.S.G.T.*)

Production of white hollow ware such as tumblers by a suck and blow process. A. SCHILLER. Ger. 567,180, Dec. 15, 1932. (*J.S.G.T.*)

Corning ribbon machine for hollow glassware. CORNING GLASS WORKS. Ger. 567,568, Dec. 22, 1932. (*J.S.G.T.*)

Blowing bottles with offset necks. H. MEIER. Ger. 567,621, Dec. 22, 1932. (*J.S.G.T.*)

Production of double-walled vessels. GLASFABRIK SOPHIENHÜTTE R. BOCK G.M.B.H. Ger. 567,781, Dec. 22, 1932. In a process for making double-walled vessels such as vacuum flasks by means of a tool working on a mass of glass in the neck of the outer vessel, means are provided for moving the work and the tool toward and away from each other both in the direction of the axis of the flask and perpendicular to it. See also *Ceram. Abs.*, **12** [2], 60; [9], 329 (1933). (*J.S.G.T.*)

Production of flashed decorated glass. BARUTHER GLASHÜTTENWERKE A.-KAISER. Ger. 567,911, Dec. 22, 1932. A layer of opal or colored glass on the inner side of a thicker clear glass wall is coated with a thinner layer of clear glass, and articles so made are decorated by cutting away the two inside layers back to the outer thick clear glass. (*J.S.G.T.*)

Press molds. N. V. MIJ. TOT EXPLOITATIE VAN UITVINDINGEN. Ger. 568,263, Dec. 29, 1932. Undivided neck molds for press and blow machines which have a circular cut-away portion to form a flange on the glass article made in them, have this cut-away portion of such dimensions that the flange breaks away when the finished article is ejected by the kick-up pin. (*J.S.G.T.*)

Glass-feeding device. EUROPÄISCHER VERBÄND DER FLASCHENFABRIKEN G.M.B.H. Ger. 568,955, Jan. 12, 1933. (*J.S.G.T.*)

Arrangement of conveyer rollers in sheet glass leers. PILKINGTON BROS. Ger. 569,586, Jan. 19, 1933. The rolls are divided into three sets, the first and third feeding the sheet forward with the correct feeding velocity while the intermediate set rotates partly with high velocity in the opposite direction and partly with still higher velocity in the feeding direction so that the sheet is fed at the necessary speed. (*J.S.G.T.*)

Molds for making double-walled vessels. E. PADBERG. Ger. 570,142, Jan. 26, 1933. In a process for blowing a single vessel in a mold and then by a plunger sliding in the lower half of the mold pushing the lower half of the vessel within the upper to form, *e.g.*, a vacuum flask, the upper mold half is furnished with a recessed portion to give the finished article an enlarged rim. (*J.S.G.T.*)

Feeding rolled sheets to the leer. PILKINGTON BROS. Ger. 570,396, Jan. 26, 1933. The adjustable bridge between the inclined guides from the rolls and the horizontal conveyer to the leer is placed so as to turn on an axis near the front edge of the conveyer so that the free edge of the bridge connects the guides. (*J.S.G.T.*)

Production of double-walled vessels. MANTLE CO. OF AMERICA. Ger. 571,172, Feb. 9, 1933. The inside and outside portions are supported in correct relation to each other, and their edges heated to softening. These are then turned toward each other and blended by means of a roller operating at the necessary angle to the axis of the vessels. (*J.S.G.T.*)

Cutting sheet glass. H. ZACH. Ger. 571,369, Feb. 9, 1933. (*J.S.G.T.*)

Partial silvering of glass surfaces. VEREINIGTE GLÜHLAMPEN UND ELECTRICITÄTS A.-G. Ger. 571,988, Feb. 16, 1933. Photocells, etc., are silvered all over by any known means and the silver layer is removed where desired by anodic solution of the silver in the glass. (*J.S.G.T.*)

Structural Clay Products

Sewer pipe and its problems. IV. A. F. GREAVES-WALKER. *Brick Clay Rec.*, **84** [3], 102 (1934).—The lack of progress in the sewer-pipe industry is due to the sluggishness of the manufacturers. Machine manufacturers are willing to help if the sewer-pipe producers will take the first step in solving their problems. The need of the glaze, an added expense, with the low absorption bodies now being produced is questioned and its elimination is suggested. For Part III see *Ceram. Abs.*, **13** [5], 118 (1934). E.J.V.

Solving the problem of mat glazes in vitrified clay sewer pipe. EUGENE C. CLEMENS. *Brick Clay Rec.*, **84** [4], 125–26 (1934).—An actual plant study was made involving the character of the glaze in salt-glazed ware produced

from a body composed of fire clay and shale of the Coal Measures of the Pennsylvania formation. The defect of matness was considered but the real reason could not be definitely fixed so a study of several glaze types was made. It was found that for the particular clay body studied, salt-glaze matness is due to the formation of crystals in the glaze. Matness increases with the degree of crystallization. The crystallization is probably promoted by the presence of CaO and MgO in some form in the glass. The composition of the crystal is partly responsible for the color of the mat salt glaze. A good salt glaze should consist chiefly of glass or glass and hematite. No definite practical remedy for the elimination of matness has been found. E.J.V.

Factors that influence drain tile in subgrade installations. F. H. ENO. *Brick Clay Rec.*, **84** [3], 91 (1934).—E. tells how to lay drain tile to take care of the effect of capillary moisture and the troublesome action of percolating waters. E.J.V.

Brick masonry. HUGO FILIPPI. *Jour. West. Soc. Eng.*, **38** [6], 345–49 (1933).—Kinds of brick and their method of manufacture, sizes of brick, face brick, strength of brick, and mortar are considered. Having determined the time-rate absorption properties of the brick being laid, F. recommends mortar-moisture control by wetting the brick sufficiently to satisfy their natural absorption in a thirty-minute period. He does not recommend adding excess water to the mortar. Properties of mortar to be considered, listed in order of importance, are plasticity and workability, volume change, impermeability, weather resistance, bond, strength, flexibility, rate of setting, freedom from efflorescence, and freedom from staining and fading. J.L.G.

Questions on the manufacture of porous brick. W. DAWIHL. *Tonind.-Ztg.*, **58** [10], 117–19 (1934).—After discussing the properties of porous brick, D. analyzes their manufacture. The required properties of raw materials, mechanical contrivances, and firing are dealt with. Materials promoting porosity, their effect, and the effect of the state of the grains is discussed on the basis of experiments. The relationship between porosity, specific gravity, and resistance to pressure is discussed. M.V.K.

Occurrence of nitrates and chlorides in brick. E. WENDERHORST. *Tonind.-Ztg.*, **58** [13], 154–55 (1934).—Methods for determining the presence of nitrates, including the diphenylamin test, the Brucin reaction, and the ferrosulfate test, are discussed. It was found that the firing temperature does not always disintegrate and expel nitrates present in brick. The presence of soluble salts in amounts of 0.01% may cause efflorescence. M.V.K.

Manganous dioxide for coloring brick. A. G. AREND. *Sands, Clays, & Minerals*, **2** [1], 41–42 (1934).—The natural buff color of a clay brick after oxidizing or the gray color after reducing can be improved by an addition of manganese dioxide making it a little more grayish brown after deoxidizing. M.H.

PATENTS

Shield for piling brick. E. J. SCHARIO. U. S. 19,121 (reissue), March 27, 1934.

Process of treating ceramic material. J. R. PARSONS (United States Gypsum Co.). U. S. 1,954,889, April 17, 1934. The process of producing a cellular clay product comprises mixing clay with water, adding to the mixture an alkaline-reacting substance to effect deflocculation of the clay, incorporating a tenacious foam with the mixture, adding thereto a reagent capable of overcoming the deflocculation and causing a delayed flocculating action so that when the flocculation occurs the foam structure will be substantially retained and the bubbles of the foam entrapped, shaping the resultant mixture into form, drying the form, and firing it.

Coloring ceramic materials. ALBERT LAMPE (I. G. Farbenindustrie A.-G.). U. S. 1,954,936, April 17, 1934. Process for coloring ceramic material consists in firing it in an atmosphere containing as the vapor of a sublimable metal chloride only the vapor of a metal chloride of the group consisting of ferric chloride, aluminum chloride, and chromium chloride, whereby the metal chloride contacts with the ceramic material and decomposes thereby depositing and fixing the corresponding metal oxide upon the surface of the ceramic material.

Hollow tile block and floor construction. F. A. HOLBY (New Jersey Clay Products, Inc.). U. S. 1,955,498, April 17, 1934.

Ventilating brick for use in cavity walls. STONEWARE, LTD., AND H. DEAN. Brit. 407,789, April 5, 1934.

Building construction or walls built of block and brick. R. A. LLOYD. Brit. 408,049, April 11, 1934.

Brick and method of reinforcing structures built therewith. A. CRUM. Brit. 408,070, April 11, 1934.

Refractories

Observations on spalling. F. W. PRESTON AND H. E. WHITE. *Jour. Amer. Ceram. Soc.*, **17** [5], 137–44 (1934).

A rapid method for the analysis of siliceous refractories. SANDFORD S. COLE AND S. R. SCHOLES. *Jour. Amer. Ceram. Soc.*, **17** [5], 134–36 (1934).

Relation between uncombined quartz and thermal expansion of ceramic bodies. W. R. MORGAN. *Jour. Amer. Ceram. Soc.*, **17** [5], 117–21 (1934).

Physical properties of ten brands of insulating refractories. W. C. RUECKEL. *Brick Clay Rec.*, **84** [3], 89–90 (1934).—A progress report of the investigation from which classifications and specifications for ceramic insulation will be developed is presented. A description of the materials used, firing temperatures, method of manufacture, service recommendations, and physical properties determined to date is given. E.J.V.

Physical properties of heat-insulating materials for temperatures above 500°C. J. S. CAMMERER. *Elektrowärme*, **4** [2], 41–45 (1934).—Heat conductivity, permanency at elevated temperatures, and compressive strength were investigated for some of the most generally used heat insulations and compiled in the following table.

Material	Density kg./m.³	Heat conductivity kg. cal./m. hr. at 100°C	Heat conductivity kg. cal./m. hr. at 500°C	Permanence vertically to heat flow up to	Compressive strength kg./cm.²
Sil-O-Cel (super)	610	0.195	0.245	1370°C	25
Sil-O-Cel (C22)	610	0.193	0.237	1100	38
Superdia	750	0.180	0.236	1350	16–20
Cristobalite	600	0.157	0.185	1160	12–15
Feuerleicht	900	0.195	0.260	1200	30
Diatomite F	700	0.170	0.230	1500	30–40

M.H.

Insulating firebrick applications on steel-heating furnaces. M. J. TERMAN. *Iron & Steel Eng.*, **11** [3], 106–107 (1934).—Characteristics of insulating fire brick essential to satisfactory performance include lightness of weight, mechanical strength, low heat flow, low thermal capacity, spalling resistance, and freedom from shrinkage. Several advantages of insulating fire brick over heavy fireclay brick linings in furnace construction are presented as follows: (1) time saved in bringing a furnace to operating temperature, ranging from 25 to 85% on a cold start, depending on size and type of furnaces, limitations on rate of heating stock, burner arrangement, and temperature control; (2) fuel savings; (3) flexibility of temperature control; (4) increase in furnace output due to uniform temperature distribution; (5) saving in floor space for the same hearth area by reduction in wall thickness; (6) improved working conditions around furnace; (7) improvement in quality of product. Data on heat flow and heat capacity of several walls are given in tabular form. A comparison of two walls of equal heat flow at thermal equilibrium shows that at a furnace temperature of 2800°F the insulating firebrick wall has a thermal capacity of 8759 B.t.u. per sq. ft., whereas the heavy wall backed up with insulation has 91,500 B.t.u. per sq. ft., a ratio of approximately 1 to 10. Several insulating firebrick installations are cited. E.J.V.

Use of super-refractories for the iron and steel industry. W. F. ROCHOW. *Iron & Steel Eng.*, **11** [3], 111–12 (1934).—Super-refractory is generally taken to mean a refractory that is appreciably better in its physical and chemical properties than the average of its class. Brick in the fireclay class which are measurably better in one or more properties than the average high heat duty fireclay brick are produced by the special selection of clays or kaolins and the addition of small amounts of more refractory high-alumina materials such as diaspore and minerals of the cyanite group. High-alumina refractories, made from diaspore and some bauxite, are becoming more extensively used in blast-furnace stoves, open-hearth checkers, water-cooled ports, etc. Magnesite brick of low iron content have decided advantages over the usual magnesite refractories for certain applications. Unfired chemically bonded magnesite brick are used with metal casings where spalling conditions are especially severe. Chrome brick of improved spalling resistance and high-temperature strength can be expected to contribute to increased service in parts of open-hearth furnaces. The scope of furnace insulation is extended with the development of lightweight refractories having high insulating value, such as the new brick suitable for use at temperatures as high as 2950°F. E.J.V.

Simplification of cupola refractories. ANON. *Bur. Stand. Simplified Practice Recommendation*, R154–34. 6 pp.—The recommendation on cupola refractories became effective March 15, 1934. This recommendation, which was proposed and developed by the industry, covers the sizes and shapes of cupola lining blocks, tap-out blocks, and slag-hole blocks. R.A.H.

Refractories in the foundry. FRANK S. RUSSELL. *Refrac. Jour.*, **10** [3], 91–93 (1934).—R. takes up the subject of patching the cupola. Patching materials are discussed and other types of lining are mentioned. Paragraphs on molding sands, steel-foundry refractories, and electric-furnace refractories are included. A.J.M.

Developments in foundry refractories. E. J. CRAWLEY. *Foundry Trade Jour.*, **50**, 71 (1934).—The paper is divided into (1) cupola linings, firebrick and monolithic, (2) crucible furnace linings, sillimanite, magnesite, and refractory concrete, and (3) molding sands, natural and synthetic. Among the monolithic linings is noted a new clay called King's earth, discovered in Northamptonshire, which is said to be peculiar for its remarkable plasticity and bonding ability. H.H.S.

Gas permeability of ceramic products at different temperatures, their laws, and their rôle on firing. PIERRE BRÉMOND. Presented at the International Ceramic Congress, Milan, 1933; abstracted in *Glashütte*, **63** [47], 793 (1933); *Sprechsaal*, **66** [52], 885 (1933); *Tonind.-Ztg.*, **57** [101], 1197 (1933).—Investigations showed that the laws of the passage of gas through ceramic products, which were known to be suitable for temperatures up to 300°, are partly suitable for higher temperature ranges. Suitable general laws may be developed with regard to the mechanism of the gas passage which will agree well with results in practice. M.V.K.

Permeability of refractory materials to gases. E. PRESTON. *Glass Rev.*, **10** [1], 10–13 (1934).—P. reviews the article by F. H. Clews and A. T. Green (*Ceram. Abs.*, **12** [12], 422 (1933)). A.A.

Practical tests on refractory cements. W. O. LAKE. *Sands, Clays, & Minerals*, **2** [1], 35–39 (1934).—Compositions of refractory cements suitable for the metallurgical industries are given. The best results were obtained with 58.02% SiO_2, 5.94 Al_2O_3, 1.6 Fe_2O_3, 0.31 TiO_2, 0.46 CaO, 0.03 MgO, 0.33 K_2O, 3.32 Na_2O, 26.39 H_2O, and 3.45 MnO_2. M.H.

Thermal expansion of silica brick. F. FROMM. *Arch. Eisenhüttenwesen*, **7**, 381–84 (1933–34); *Stahl & Eisen*, **54**, 84 (1934).—Samples of silica brick were investigated, the specific weight ranging from 2.38 to 2.44 g. per cm.³ The samples were heated to 1600°C. The thermal expansion between 0 and 1600°C increases considerably with an increasing specific weight. The same is true for the permanent after-expansion occurring at temperatures above 1400°C. The after-expansion may be reduced by placing the sample under pressure while heating. This result is explained by a decrease in porosity. It is proposed to carry out standard tests under conditions similar to actual service conditions, *i.e.*, under load. All samples show the same specific weight of 2.32 after heating to 1600°C. The porosity of samples heated without load increases with the temperature, the increase being larger for samples with a high specific weight at room temperature. W.M.C.

Measuring the coefficients of conductivity of refractory

materials. L. LONGCHAMBON. Presented at the International Ceramic Congress, Milan, 1933; abstracted in *Sprechsaal*, **66** [52], 886 (1933); *Glashütte*, **63** [47], 793–94 (1933).—The difficulties of this measurement lie in the determination of the temperature of the hot and cold side of the sample. They were solved in the following manner: The temperature of the hot side was measured by an optical pyrometer which was observed through a hole in the middle of the electric heating plate which heats the surface of the sample. The temperature of the cold side was measured by its radiation on a thermoelement, while the amount of heat transmitted was determined with a water-circulating calorimeter. The coefficient of thermal conductivity was exactly determined to hundredths. See also *Ceram. Abs.*, **13** [4], 90 (1934). M.V.K.

New method for producing highly refractory mixes. WALTER PETERS. *Feuerungstechnik*, **22** [2], 24–25 (1934).—Mixtures containing the oxides of magnesium, aluminum, chromium, and silicon are mixed in such a proportion that the sum of the gram molecules of magnesia is equal to or exceeds the sum of the gram molecules of alumina and chromium oxide; the quantity of chromium oxide must be larger than that of alumina. The mixture is fired in an electric furnace above its melting point. The products obtained are dense and resist high temperatures and attacks of acid and basic slag. M.V.K.

Firing magnesite brick. J. H. CHESTERS AND C. W. PARMELEE. Presented at meeting of English Ceramic Society, Nov., 1933, London; *Colliery Guard.*, **147** [3806], 1097 (1933); see also *Ceram. Abs.*, **13** [3], 62 (1934). E.J.V.

Studies of refractory minerals. XVII. Magnesite. ANON. *Refrac. Jour.*, **10** [3], 125 (1934).—The occurrence and properties of magnesite are described. For Part XVI see *Ceram. Abs.*, **13** [5], 121 (1934). A.J.M.

Firing silica brick. RICH. PRESTIN. *Tonind.-Ztg.*, **58** [14], 167–68 (1934).—The increase in temperature above 1400° must be very slow when firing silica brick, because at this temperature range the quartzites undergo the largest conversion. It is always advantageous to fire the brick as long as possible at cones 14 to 16. M.V.K.

Softening temperature of ordinary silicoaluminous refractory products. I. MARCEL LÉPINGLE. *Verre & Silicates Ind.*, **5** [2], 21–26; [3], 42–43; [4], 64–68 (1934).—Conditions affecting the softening temperature of silicoaluminous refractories are discussed in detail. Data on the composition and properties of German, English, Japanese, French, and Belgian refractories are tabulated and discussed. M.V.K.

High-grade refractories. J. WINNING. *Blast Fur. Steel Plant*, **22** [3], 180–81 (1934).—W. points out the qualities of 40 to 45% alumina refractories when regarded as an ideal refractory material. E.J.V.

Recent progress in the manufacture of industrial refractory materials. DANIEL PETIT. Presented at the Congress of Industrial Heating, Paris, 1933; abstracted in *Rev. mat. constr. trav. pub.*, No. 292, pp. 14–15 (1934).—Refractories may be classified as (1) silicoaluminous and aluminous products with an alkali content up to 45%, (2) siliceous products containing 92 to 100% silica, and (3) special products, with a bauxite, sillimanite, corundum, silicon carbide, or chromite base. A special group consists of refractory cements, flue linings, and refractory insulating materials. The progress achieved in their manufacture is due to the method of "supercompression." The principle is that 90 to 95% of the fired refractory material, 5 to 10% bonding agent, and very little water are compressed at high pressure in steel molds. The drying time is considerably reduced; the material, having had a preliminary firing, shrinks little on drying and firing and does not tend to crack and deform. The resistance under load at high temperature is considerably increased and the refractories resist chemical attack much better. This method of supercompression may be applied to all kinds of refractories. The properties and conditions of use of various refractory linings, special cements, and insulating materials are enumerated. M.V.K.

Special super-refractories. MAIRE. Presented at the Congress of Industrial Heating, Paris, 1933; abstracted in *Rev. mat. constr. trav. pub.*, No. 292, pp. 15–16 (1934).—The characteristics of refractories may be classified as follows: (1) from the mechanical viewpoint: resistance to pressure, flection, abrasion, and sharp and repeated variations of temperature; (2) from the physical viewpoint: specific heat, thermal conductivity, density, porosity, permeability, linear dilatation, shrinkage or expansion of volume after heating, electrical conductivity, etc.; (3) from the chemical viewpoint: elementary and rational analyses, resistance to chemical action in contact with materials such as slag, glass, gas, dust, metallic bath, etc. Refractories may be classified into (*a*) products composed of clay (hydrated aluminum silicate), (*b*) products composed of acids or oxides (silica, zirconia), (*c*) basic products (magnesia, dolomite), (*d*) neutral products (alumina), (*e*) mixtures of oxides, (*f*) chromite, sillimanite, cyanite, and carbon in the form of graphite, and (*g*) refractories produced from chemical compounds obtained industrially in electric furnaces, such as those having a carbide base: silicon, tungsten, molybdenum, and titanium carbides. The properties, manufacture, and use of silicon carbide and fused alumina are discussed. Spinel (MgO, Al_2O_3), oxides of magnesium, zirconium, and thorium, mullite ($3Al_2O_3 \cdot 2SiO_2$), etc., also belong to the group of super-refractories and are used when it is important to avoid any risk of oxidation or chemical attack. See also *Ceram. Abs.*, **13** [5], 120 (1934). M.V.K.

Refractories and the clay products industry. W. E. PATTERSON. *Can. Chem. Met.*, **18** [3], 52 (1934).—General properties required in refractories and the use of different types of refractory materials are discussed. Plastic fire brick is of special utility for patching and for the construction of door arches, burner ports, and fire arches when, by its use, the services of a skilled tradesman may often be unnecessary. Proper use of refractory bonding mortars and the place of refractory concretes in construction, subject to comparatively low temperatures, are also discussed. E.J.V.

Recent progress in the manufacture of refractories. ANON. *Jour. four élec.*, **43** [2], 59–60 (1934).—A brief review is given of the progress made during the last few years in the manufacture of refractories in France. G.R.S.

Progress in refractories. ANON. *Times Eng. Supp.*, **33**, xviii (Jan. 27, 1934).—This issue contains an annual review of engineering trades. The enterprise of smaller firms making refractories is noted. The importance of mullite in fire brick is recognized; steps are now taken for its artificial production. Other subjects considered are research, specification revision, raw materials, electric furnaces, thermal insulation, foundry sands, and coöperation. H.H.S.

"Longenecker" interlocking furnace arch. BASIC INDUSTRIES EQUIPMENT CO., LTD. *Iron Coal Trades Rev.*, **127** [3423], 515 (1933).—A flat suspended arch of interlocking tile arranged to facilitate repairs is described. Illustrated. W.E.R.

Refractory alumino-silicates of tank furnaces. FRANCESO BOELLA. Presented at the International Ceramic Congress, Milan, 1933; abstracted in *Sprechsaal*, **66** [52], 885 (1933); *Glashütte*, **63** [47], 793 (1933).—Chemical composition and porosity greatly affect the stability of refractory products; stability is especially high with a high alumina content and a low porosity. The disintegration of tank-block joints depends on the penetration of the liquid glass in the hollow spaces between the blocks; this leads to an increase of the surface of attack and an increase of the temperature of the blocks. Experiments showed that this destruction may be greatly lowered by polishing the joints between the blocks. M.V.K.

Refractory linings without joints. F. SAINTENOY. Presented at the Congress of Industrial Heating, Paris, 1933; abstracted in *Rev. mat. constr. trav. pub.*, No. 292, p. 16 (1934).—Such mixes have a low water content, a great plasticity, and low shrinkage; they harden after firing to 800 or 1000°. These products (used chiefly in the U. S.) have 25 to 43% alumina and 1 to 2.5% iron peroxide. Their hardness is from 3 to 4.5 (Mohs); the working temperature is between 1000 and 1700°. M.V.K.

Recuperator on air furnace. ANON. *Foundry*, **62** [2], 11 (1934).—The advantages obtained from the use of a recuperator on a pulverized coal-fired metal melting unit are described and illustrated. The recuperator consists of rows of horizontal silicon carbide refractory tubes supported at either end in terminal walls of fire clay. Air to be heated is drawn through the tubes and the combustion gases pass around them. Fireclay corebusters are centered in the tubes to keep the air in contact with the walls of the tubes. F.G.H.

Grecian emeries and bauxites. JACQUES DE LAPPARENT. *Compt. rend.*, **197** [1], 75–77 (1933).—Recent investigations seem to confirm the view that emeries from Naxos and Samos are ancient bauxites which have been formed under the once tropical conditions of the Mediterranean countries while in the northern climates glacial formations, "tillites," were deposited. M.H.

Principal Italian magnesite deposits. G. CASTELLI. *Ind. Min.*, No. 5, pp. 189–95 (1933); abstracted in *Bibliografia Italiana* [Series C], **6** [11–12], 41 (1933).—C. indicates principal localities and production figures for Italy. H.F.V.

BOOK AND BULLETINS

Materials Testing in the Iron and Steel Foundry (Werkstoffpruefung in der Eisen und Stahlgiesserei). G. TSCHORN. Wilhelm Knapp, Halle (Saale), Germany. 196 pp. Reviewed in *Foundry*, **62** [2], 52 (1934).—A chapter which includes the chemical analyses of fuels, slags, limestones, dolomite, fluorspar, and refractories is contained in this volume. F.G.H.

Refractories fellowship at Mellon Institute. F. A. HARVEY. *Amer. Refrac. Inst. Tech. Bull.*, No. 46, 12 pp. (1934).—H. explains the functions and facilities of the Refractories Fellowship which is maintained by the American Refractories Institute at Mellon Institute of Industrial Research. The sectional headings are personnel, general, testing equipment and methods, special tests, consulting work, and conclusion. Under testing equipment and methods he describes determination of pyrometric cone equivalent, load test, reheating test, cold crushing strength and modulus of rupture, and spalling tests; under special tests, thermal expansion, effect of gases on refractories, permeability determinations, studies of clays, photographic service, petrographic and X-ray studies, and specifications. Available information is given to members of the A.R.I. without charge. In general, tests are made at cost. The benefits to be derived warrant wide use of the facilities of the Fellowship. W.E.R.

Calculation of heat losses through furnace walls. R. H. HEILMAN. *Amer. Refrac. Inst. Tech. Bull.*, No. 47, 8 pp. (1934).—H. presents a method he has developed to calculate the rate of transfer of heat by conduction through walls of furnaces. The method is applicable to walls composed of refractory brick or combinations of refractory brick and insulation. Data required for the calculations are given, together with references to additional published data. The paper includes brief explanations of factors which affect the rate of transmission of heat to, through, and from such walls. W.E.R.

Trade-marks in the refractory and furnace building industries. L. LITINSKY. Published by Litinsky, Leipzig, 1934. Price 6.00 Rm. Reviewed in *Feuerungstechnik*, **22** [2], 27 (1934); *Verre & Silicates Ind.*, **5** [4], 74 (1934).—The development of new and special products under different names often produces confusion. L. has collected and classified in alphabetical order about 1500 trade-marks or special denominations relative to refractory products and industrial furnaces. German and foreign industries are reviewed. An appendix gives the complete technical literature of industrial furnaces, an index of principal technological expressions, and a list of technical and scientific publications. See also *Ceram. Abs.*, **13** [2], 50 (1934). M.V.K.

PATENTS

Refractory cement. G. F. COMSTOCK (Titanium Alloy Mfg. Co.). U. S. 1,952,119, March 27, 1934. A refractory, slag-resistant cement containing substantially by weight dead-burned, finely ground magnesite 50 parts, electrically fused, finely ground magnesia 15 parts, refined zircon sand (60-mesh) 25 parts, and refined zircon milled (300-mesh) 10 parts, bonded with sodium silicate solution of specific gravity of about 1.3, wherein magnesite shrinkage is counteracted by expansion of magnesia-zircon compounds formed when the cement is fired at

temperatures up to 2900°F to volatilize the binder and coalesce the particles thereof.

Refractory and method of making. G. F. COMSTOCK (Titanium Alloy Mfg. Co.). U. S. 1,952,120, March 27, 1934. A refractory comprising principally coarse-grained calcined magnesite, the particles of which are capable of passing through a 4-mesh screen, fired and bonded with relatively finely divided particles of fusible zircon-magnesite compound to coalesce with the magnesite grains at about 2800°F.

Fire wall. MICHAEL LIPTAK. U. S. 1,952,175, March 27, 1934.

Chemical treatment of clays. W. S. WILSON (Merrimac Chemical Co.). U. S. 1,953,144, April 3, 1934. (1) The method of extracting alumina which consists in calcining natural clay fragments having a hard rock-like texture that is not readily dispersed in an aqueous medium and substantially free of ground particles, subsequently treating such calcined clay with an aqueous inorganic acid contaminated with colloidal or finely divided carbonaceous impurities whereby the alumina present therein is dissolved by the mineral acid while the colloidal or finely divided impurities present in the mineral acid are adsorbed by the silica residue of the clay fragments, and thereafter separating the resulting aqueous aluminum salt solution from the silica residue. (2) The siliceous residue of sludge acid extracted calcined flint clay fragments having absorbed thereon carbonaceous impurities from sludge acid.

Checkerwork construction. A. L. FOELL. U. S. 1,953,342, April 3, 1934.

Basic refractory and method of making. C. E. WILLIAMS AND J. D. SULLIVAN (Battelle Memorial Institute). U. S. 1,954,552, April 10, 1934. A basic refractory material is composed of barium monoxide and magnesium oxide.

Highly refractory mass and process of producing. ARTHUR SPRENGER. U. S. 1,954,715, April 10, 1934. A process for the production of highly refractory masses which comprises smelting raw materials containing the oxides of chromium, aluminum, and magnesium in such a manner that the resulting product is composed of at least 80% of chromium oxide, aluminum oxide, magnesium oxide, and iron oxide in the proportion of the formulas of their spinel formations, $MgO \cdot Cr_2O_3$, $FeO \cdot Cr_2O_3$, $MgO \cdot Al_2O_3$, and $FeO \cdot Al_2O_3$, and in which there are, of the basic oxides, at least 4 moles of MgO to 1 mole of FeO and of the acid oxides, not over 8.5 moles of Al_2O_3 to 1 mole of Cr_2O_3, the remainder of the product containing a maximum of 15% silicic acid counted on the basis of the total mass.

Furnace wall. B. H. SNOW (Bernitz Furnace Appliance Co.). U. S. 1,955,700, April 17, 1934.

Wall construction. W. D. DREISKE. U. S. 1,955,706, April 17, 1934.

Fire brick for domestic fireplaces. B. DINELEY. Brit. 406,729, March 14, 1934.

Terra Cotta

Decay of building stones through soot. ARTHUR R. WARNES. *Sands, Clays, & Minerals*, **2** [1], 17–18 (1934).—Soot is a contributory cause of decay of stones because of the presence of free H_2SO_4, ammonium sulfate, and ammonium chloride. A typical analysis of (London) soot showed 47.50% C, 4.39 H, 5.63 N, 20.25 ash, 15.30 tar, 2.26 S, and 6.35 Cl, with an acidity of 0.60%. Soot removed from stones contained, besides the two ammonium salts, considerable quantities of calcium sulfate which is the principal by-product of limestone decay. The ever-present moisture materially assists in the decay. M.H.

Terra sigillata problem. BERDEL. *Sprechsaal*, **67** [5], 59 (1934).—The real terra sigillata has never been fired to higher temperatures than 900 to 950° and its luster was obtained only by using borates. M.V.K.

PATENTS

Method of producing earthenware. PATTILLO HIGGINS. U. S. 1,952,757, March 27, 1934. The method of producing light, porous earthenware which consists in heating a natural earth formation, which fuses at a low temperature, to the fusing point to generate gas therein to form pockets or voids throughout the mass, then pouring the melted substance into a mold to mold the same to the desired shape, and permitting it to set in final form in the mold.

Building construction. A. F. BEMIS (Bemis Industries, Inc.). U. S. 1,953,287, April 3, 1934.

White Wares

Effect of mechanical pressure on the drying and firing properties of typical ceramic bodies. A. E. R. WESTMAN. *Jour. Amer. Ceram. Soc.*, **17** [5], 128–34 (1934).

Electrical conduction and diffusion in nonmetallic solid substances. C. TUBANDT. *Z. Elektrochem.*, **39** [7*b*], 500–506 (1933).—In addition to direct measurements of conduction, the formulation of laws of conduction requires the results of investigations of transport relations, diffusion, the Ludwig-Soret effect, and the thermoelectric properties. As the result of conduction measurements solid electrolytes can be separated into three groups: (1) compounds whose conduction follows the van't Hoff exponential equation with a straight-line temperature-conduction relation; (2) those for which the two-membered Smekal equation is satisfactory, with a discontinuous temperature-conduction curve; and (3) compounds whose temperature-conduction curves can not entirely or in part be expressed in an equation. Transference measurements are discussed. The results of measurements of conduction and transference may be controlled by diffusion measurements since con-

duction and diffusion are parallel properties. When partial electronic conduction occurs the diffusion method is of importance. E.J.V.

Electrical conduction in solid substances at high field strengths. A. v. HIPPEL. *Z. Elektrochem.*, **39** [7*b*], 506–12 (1933).—The question of the limit of validity of Ohm's law is discussed by analogy to the results of measurements of electrical conduction in nonmetallic crystals of high field strength. Heat and electrical breakdown, two processes in the breakdown of a dielectric, are characterized. These processes were investigated microscopically with crystal lamellae under 70 atmospheres pressure. Sharp breakdown tracks about 0.01 mm. wide, characteristically oriented corresponding to the polarity of the field and to the crystal structure, appeared with a geometrically homogeneous electrical field. General rules, derived from an investigation with the alkali halides, are given and explained for the special case of NaCl. An impact ionization theory of electrical breakdown is justified by the experimental results. E.J.V.

Measuring stresses as a detection of expansion due to moisture. GÜNTER HAMMER. *Keram. Rund.*, **41** [47], 621–25 (1933).—The measurement of stresses according to Steger shows what stresses appear between the body and glaze after a certain length of time. This change is based on an increase in volume of the body due to moisture. Experiments showed that the supplementary hair cracks are chiefly produced by a change in volume of the body and depend much less on the differences in the thermal expansion between the body and glaze at different temperatures. Illustrated. M.V.K.

Research work on pottery casting slips. HARRY W. WEBB. Presented at meeting of the English Ceramic Society, Stoke-on-Trent, Feb. 12, 1934; abstracted in *Pottery Gaz.*, **59** [681], 333–37 (1934). E.J.V.

History of the ceramic industry. III. R. D. *Rev. belge ind. verrières, céram., émail.*, **4** [11], 248–51 (1933).—A brief review of (1) fine English faience, (2) stoneware, (3) soft French porcelain, (4) soft English porcelain, (5) mixed porcelain, (6) hard porcelain, (7) porcelain of Saxony, and (8) the hard porcelain of Sèvres is given. For Parts I–II see *Ceram. Abs.*, **13** [1], 3 (1934). M.V.K.

Royal Copenhagen porcelain factory. ANON. *Danish Foreign Office Jour., Commercial Rev.*, **13**, 171–75 (1933).—Founded in 1775, the first artists coming from Meissen, the factory went into private ownership in 1867. A new undecorated but colored "Bremerholm" faience is illustrated. H.H.S.

Industrial revolution in the potteries. JOHN THOMAS. *Pottery Gaz.*, **59** [682], 492–99 (1934).—The story of how the production of pottery in North Staffordshire was converted from a village occupation into a consolidated industry is told. E.J.V.

Improving organization of the English pottery industry. ANON. *Times Eng. Supp.*, **33**, 448 (1934).—The National Council of the Pottery Industry has referred a number of suggestions for closer organization to the two sections of the industry, manufacturers and operatives. H.H.S.

English pottery industry: number of operatives. ANON. *Times Eng. Supp.*, **33**, 426 (1934).—The Home Office reports that 32,149 males and 31,329 females were employed in the industry in 1933. H.H.S.

PATENTS

Dental investment composition and process. P. F. COLLINS (Columbus Dental Mfg. Co.). U. S. 1,953,075, April 3, 1934.

Insulator. W. L. STINSON AND C. L. STROUP (Jeffrey Dewitt Insulator Co.). U. S. 1,952,517, March 27, 1934.

Toilet bowl. H. S. DE MALAUSSENE (Adolph L. Bernheimer). U. S. 1,955,579, April 17, 1934.

Insulator. D. H. ROWLAND (Locke Insulator Corp.). U. S. 1,955,609, April 17, 1934.

Manufacture of spark plugs. A C SPARK PLUG Co. Brit. 407,275, March 21, 1934.

Spark plugs. A C SPARK PLUG Co. Brit. 407,282, March 21, 1934.

Teapots, coffee-pots, etc. J. TURTON & Co., LTD., AND A. KETTERER. Brit. 408,080, April 11, 1934.

Combined teapot and stand. H. COWAN. Brit. 408,081, April 11, 1934.

Production of ceramic liquid resistances. PORZELLANFABRIK KAHLA. Brit. 408,123, April 11, 1934.

Equipment and Apparatus

Universal color-measuring apparatus. K. FISCHER. *Z. Instrumentenk.*, **51** [7], 347–60 (1931).—A spectrumphotometer of simpler and shorter construction than usual is described. A color is determined according to its contents of black and white and color proper. The methods are explained in detail for the use of the instrument as spectrograph and photometer and for measuring brightness and gloss and color effects of coats of paint. M.H.

Theory and applications of the Mach-Zehnder interference refractometer. H. SCHARDIN. *Z. Instrumentenk.*, **53** [9], 396–403; [10], 424–36 (1933).—Principle and theory of the instrument is explained and the occurrence of interference stripes is discussed. Monochromatic light is preferable, but white light can also be used in the measurements. The dislocation of the stripes is a measure of the refractive index which can be used for determining density, pressure, or temperature of gases. A few examples illustrate the method. M.H.

New universal refractometer with internal scale. P. LOB. *Z. Instrumentenk.*, **53**, 27–30 (1933). (*J.S.G.T.*)

Tests on a photoelectric polarimeter. G. BRUHAT AND P. CHATELAIN. *Rev. d'Optique*, **12**, 1–20 (1933).—The monochromator, polarimeter, and amplifier of a photoelectric polarimeter incorporating quartz lenses are described in detail. The method of using the instrument together with its accuracy and possible sources of error is discussed. (*J.S.G.T.*)

Integrating photometer for X-ray crystal analysis. B. W. ROBINSON. *Jour. Sci. Instruments*, **10** [8], 233–42

(1933).—A photoelectric photometer designed for the measurement of integrated X-ray intensities in crystal-analysis photographs is described. All parts could be built by an intelligent mechanic since none is carefully finished. The only expensive parts are two photocells and one amplifying valve. Good agreement was obtained between results secured photographically with the instrument and those secured from ionization measurements. The theories underlying the photometer and its construction and use are explained. Illustrated. J.L.G.

"Electric eye" device insures efficient combustion. Ess Instrument Co. *Gas Age-Rec.*, **73** [12], 292 (1934).—The "Haze-gage," designed to measure the haze density of combustion gases and thereby afford a definite means of combustion control, operates by means of an "electric eye" and utilizes the principle of a definite haze point (registered by the instrument on a dial) for every fuel-air mixture, type of furnace, and operating characteristic. When the haze-density coefficient corresponding to correct combustion is too light or too dark, a visible or audible signal is given. A meter is provided giving continuous indication of haze. A red light indicates deficiency of air, and a green light excess air. Illustrated. E.J.V.

Electricity in the brickmaking industries. H. V. Henniker. *World Power*, **21** [123], 123–28 (1934).—After a brief outline of the various steps in the brickmaking process, H. takes up the character of the drives necessary to operate the different pieces of machinery used in each step. The necessary auxiliary drives, though not involved in any direct step in the process, are listed, and advantages of electric power for them are enumerated, *e.g.*, greater efficiency of the electric motor, greater regularity of operation, less space required for the power sources, etc. Illustrated. E.J.V.

Construction of spectrographs of large illuminating power. A. C. S. Heel. *Rev. d'Optique*, **12**, 49–69 (1933). (*J.S.G.T.*)

Measurements of thickness with the microscope. P. Metzner. *Z. Instrumentenk.*, **51** [5], 243–47 (1931).—The method is described and the sources of error to be avoided are pointed out in particular. An accuracy of 5% can easily be obtained; strong magnification and the aperture of the objective lens are recommended. M.H.

Wear-resisting nozzles for sandblast jets. H. Gge. *Glas & App.*, **14** [8], 59 (1933).—Nozzles of sandblast jets are lined with tungsten carbide which increases the life of the nozzle considerably and is, in spite of its higher price, economical in operation. M.H.

Loss of pressure in curved parts of pipe lines for compressed air. E. Stach. *Glückauf*, **67** [45], 1400–1404 (1931).—T-pieces with straight passage and rounded-off branch gave best results, and the elbow with a radius of curvature 3 times the elbow diameter has the best value if its diameter widens circularly toward the center from the two ends. Charts show numerical figures for the losses. M.H.

New method for determining humidity of sands. Anon. *Rev. fonderie moderne*, **27**, 259–60 (1933).—The apparatus consists of an autoclave in which the sand to be tested is mixed with calcium carbide; the reaction, $2H_2O + CaC_2 = Ca(OH_2) + C_2H_2$, takes place and the pressure of the developed acetylene gas is an indication of the humidity contained in the sand. An attached manometer can be calibrated in % H_2O. An exact description of the procedure is given which applies to other substances similar to sand. M.H.

Elutriation as an aid to fine grinding. A. L. Curtis. *Sands, Clays, & Minerals*, **2** [1], 21–26 (1934).—The kinetic elutriator of Andrews was tested with regard to its effectiveness in determining the efficiency of a grinding process. After 10 grinds (about 5 hr.) 90% of the ground material passed a 200-mesh sieve. The tests showed clearly that the presence of very fine particles in a mill have a detrimental effect on the reduction of coarse and medium grains present by forming a cushion which resists the action of further grinding. The fine particles should therefore be continuously removed by hydraulic or pneumatic methods in order to increase the efficiency of the mill. M.H.

New apparatus for determining size distribution of particles in fine powders. R. T. Knapp. *Ind. Eng. Chem., Anal. Ed.*, **6** [1], 66–71 (1934).—The "microneter," based on the sedimentation principle, is described in detail. Illustrated. F.G.H.

Unitized gas-analysis apparatus. M P. Matuszak. *Ind. Eng. Chem., Anal. Ed.*, **6** [1], 72–78 (1934).—Constant-pressure gas analysis equipment has been devised which utilizes the advantages and discards the disadvantages of the Hempel and Orsat systems, combining the flexibility and adaptability of the one with the convenience, compactness, and rapidity of the other. The apparatus consists of complete self-contained units that fasten together to form any desired assemblies of the Orsat type. Improvements have simplified gas-analysis equipment and its manipulation and increased its accuracy, convenience, and usefulness. Illustrated. F.G.H.

Coreless induction furnace for multiphase current of low frequency. W. Hessenbruch and W. Rohn. *Stahl & Eisen*, **54** [4], 77–82 (1934).—A coreless induction furnace is described which is operated directly from the city supply. The lining is formed from fused magnesia and sintered in the furnace. The furnace may be used up to 1800°C. Experiments were carried out on the flow of the melt. It was found that the lining will not be washed out by the action of slag. Metal and slag may be mixed thoroughly in this furnace allowing a high rate of melting and fining. By decreasing the motion of the melt during the fining period a rapid desulfurizing and deoxidizing is obtained. It is possible to melt an iron of 99.95% iron content. Chromium nickel steel of 18% chromium and 8% nickel content may be decarburized to less than 0.02% carbon content. Data presented show the great economy of this type of furnace. W.M.C.

Portable calorimeter of the Junkers Company. W. Wunsch and H. Seebaum. *Gas. & Wasserfach*, **75** [32], 644–47 (1932).—An instrument for measurements under operating conditions and for routine measurements is described which is independent of water connection and can be used anywhere. Several examples of determinations of heating values are given; the instrument is independent of temperature fluctuations. M.H.

Special applications of industrial electric heating. G. Gobbers. *Elektrowärme*, **4** [3], 56–58 (1934).—Con-

struction and heating elements of box-type, multiple, and melting furnaces with built-in or suspended heating elements are described. M.H.

Theory of drying. IV. G. BARBEROT. *Rev. mat. constr. trav. pub.*, No. 291, pp. 222–28*B* (1933).—Formulas and diagrams are developed. For Part III see *Ceram. Abs.*, **13** [3], 68 (1934). M.V.K.

Correcting drying and firing troubles. ANON. *Brick Clay Rec.*, **84** [4], 131–32 (1934).—Called in to correct losses due to cracking of ware, the author first made a check on the temperatures on the inside and outside of special pieces and showed that the drier was being inefficiently heated. On correcting conditions in the drier and installing a carriage for carrying the heavy special pieces during drying the drying cracks were eliminated. The larger and smaller pieces were segregated in the drier. By correcting the draft in the kiln, arranging for careful firing, and holding the kiln at a soaking temperature of 2150°F a lower fuel consumption and harder fired product resulted. E.J.V.

Measurement of humidity in industrial plants. FR. LIENEWEG. *Siemens-Z.*, **11** [1], 26–32 (1931).—Devices for measuring and controlling humidity for high and low temperatures are described. M.H.

New humidity drying method for the heavy clay ceramic industry. OTTO PHILIPP. *Tonind.-Ztg.*, **58** [11], 134–36 (1934).—Data on the new method of drying are given. Illustrated. M.V.K.

New method for heat radiation measurements. W. KOCH. *Z. tech. Physik*, **15** [2], 80–82 (1934).—The surface, *A*, to be measured is kept at room temperature. The second surface, *B*, is heated to 100° and placed in front of *A*. From the amount of heat used to keep *B* at 100° the heat radiation may be calculated. For calibrating the instrument, polished or blackened aluminum sheets of known radiation behavior or sheets covered with parallel black stripes are used. Results obtained check well with results of other methods. W.M.C.

Heat liberation from boiler fuel. E. W. ROBEY AND W. F. HARLOW. Presented before the Institution of Mechanical Engineers; abstracted in *Iron Coal Trades Rev.*, **127** [3435], 988–89 (1933).—From data published by the U. S. Bureau of Mines the authors develop that efficient admission of secondary air would permit thicker fuel beds than have previously been adopted as a basis of stoker design; hence the width of stokers may be reduced and narrower boilers used, which would in turn permit higher gas velocities in the convection tubes of boiler and superheater. W.E.R.

Thermal apparatus and measurements. I. F. HENNING. *Physik*, **2** [1], 1–10 (1934).—Present developments tend to eliminate the observer and to record permanently the data of the experiments. The following thermal properties are reviewed: thermal expansion, small vapor pressures, calorimetric investigations, low temperatures, fundamental points for thermometers, resistance thermometers, thermocouples for high temperatures, high temperatures, heat-radiation pyrometers, temperatures of heated gases and flames, and heat radiation. W.M.C.

Cross-thread pyrometer, a new partial radiation pyrometer. H. GRUESS AND G. HAASE. *Siemens-Z.*, **11** [6], 297–301 (1931).—The brightness of the radiating body to be measured is compared with the brightness of the filament at definite temperature by photometration with a gray wedge. Temperatures between 900 and 1800°C can be measured. M.H.

Thermocouples for temperatures up to 2000°. W. C. HERAEUS G. M. B. H. *V. D. I. Nachrichten*, No. 11 (1933); abstracted in *Verre & Silicates Ind.*, **5** [3], 54 (1934).—A thermoelement resistant to a temperature of 2000° has been constructed. One branch is made of iridium, the other of an alloy (60% Rh and 40% Ir). The protecting pipes contain corundum, magnesia, zirconium, and thorium oxide. M.V.K.

Gearless crushing machine. ANON. *Mech. World*, **95** [2464], 273–74 (1934); *Metallurgia*, **9** [53], 147–48 (1934).—This vertical gearless drive gyratory crusher is an ingenious application of the cam method of speed reduction. The relatively high speed of the driving motor is reduced by gyratory and rolling motions to a low speed at the crushing member with correspondingly high increase in force. Illustrated. E.J.V.

Experiments with the working of the wind-sifter tube mill. FR. PROCKAT. *Tonind.-Ztg.*, **58** [11], 131–33; [12], 143–45; [13], 156–58; [15], 184–85 (1934).—The characteristics of a wind-sifter tube mill are described and the effect of wind sifting on the grinding process is discussed. Illustrated. M.V.K.

New insulating medium. S. S. KISTLER. *Heating & Ventilating*, **31** [4], 55 (1934).—"Silica aerogel," a new insulating medium, is an impalpably fine webwork of purest sand interlocked with air and extremely light in weight. E.J.V.

Design of "Dustop" air filter. D. C. SIMPSON. *Ind. Eng. Chem., News Ed.*, **11** [20], 303–304 (1933).—Principles of design involved in the construction of air filters using glass wool packing are described and illustrated. F.G.H.

Cotton for filtration in the ceramic industry. ERICH WALLA. *Sprechsaal*, **67** [8], 106–109 (1934).—Attempts to replace cotton by other materials such as leather, etc., for filtering and different cotton weaves of cloths for filters are discussed. Illustrated. M.V.K.

The "bite" of rolls. E. DANN. *Arch. Eisenhüttenwesen*, **6** [12], 539–41 (1933).—An equation is derived for the angle of biting based on the coefficient of friction, angle of friction for the gliding motion, and the force of resistance of two rolls. Equations are presented for an angle of 90° and for smaller angles. The influence of the velocity of the rolls on the coefficient of friction is derived. The ratio of average and maximum pressures is of great importance, the ratio being different for different cross-sections of the sample. The influence of the surface roughness of the rolls and that of different types of grooves were determined. W.M.C.

BOOKS AND BULLETINS

Electrical Engineering Practice. Vol. III. J. W. MEARES AND R. E. NEALE. Chapman and Hall, London. 920 pp. Price 25s net. *Can. Engr.*, **66** [13], 30 (1934).—This volume takes up the applications of electrical energy and treats of motors and their control, electrical drives, hoisting, conveying, electricity in mining, agriculture

and traction, the propulsion of ships, and chemical and metallurgical processes. E.J.V.

The Chemical Engineer. Vol. III, Part III. Measurement of Physical Conditions in Industry (Der Chemie-Ingenieur. Band III, Teil III. Messung von Zustandsgrossen im Betriebe). A. EUCKEN AND M. JAKOB. Akademische Verlagsges. m. b. H., Leipzig, 1933. 275 pp. Price 26 M, bound 28 M. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [3], 53 (1934).—The measurement of physical conditions of industrial operation is presented not only from the theoretical and mathematical viewpoint, but also from a practical standpoint. The operation of continuous and automatic instruments is described clearly. The accuracies of each type, as well as sources of error due to incorrect use as to location and unsatisfactory conditions, are included in the discussions. Illustrated. Bibliography. F.G.H.

Review of fine grinding in ore concentrators. A. M. GOW, M. GUGGENHEIM, AND W. H. COGHILL. *Bur. Mines Information Circ.*, No. 6757, 29 pp.—This report summarizes and compares data on fine-grinding practice in ore-concentrating plants throughout the U. S., Alaska, Canada, Mexico, and Cuba. See also *Ceram. Abs.*, **13** [4], 95 (1934). R.A.H.

Measurement of humidity in closed spaces. *Dept. Sci. Ind. Research*, Special Rept., No. 8. H. M. Stationery Office; London. 70 pp. Price 50¢. Abstracted in *Heating & Ventilating*, **31** [4], 33 (1934).—A comprehensive discussion of the methods for humidity measurement and control finding practical application is given. Methods for controlling relative humidity in enclosed spaces include the water-spray method, the calcium chloride method, the sulfuric acid method, Lindley's method, utilizing revolving plates saturated with sulfuric acid, and construction and manipulation of an enclosure for the calibration of hygrometers. The principles underlying the water-spray method are discussed in detail, and a description of its application to the design of a laboratory drying kiln is given. The chemical method is established as the ultimate standard of reference for measurement of humidity. This is accomplished by the determination of the increase in weight of a quantity of moisture-absorbent material when a measured quantity of air is aspirated through it. An improved hygrometer, designed by Rideal and Hannah, applies this principle to the hygrometric measurements and eliminates the inaccuracies and tedious labor formerly involved in these determinations. The general classifications of wet- and dry-bulb hygrometers of the ventilated type, the dew-point hygrometer, and the hair hygrometer are taken up in detail, with descriptions of important forms and variations in which these principles are applied. Concluding sections deal with apparatus for the study of the change of length of materials subjected to a cycle of humidities, a hygrometer employing glycerine, the effect of humidity on the relative mobility of ions, a fog-formation hygrometer, the hot-wire hygrometer, and the measurement of humidity up to a temperature of 212°. E.J.V.

PATENT

Opacimeter and method of measuring opacity. M. N. DAVIS (Paper Patents Co.). U. S. 1,950,975, March 13, 1934.

Kilns, Furnaces, Fuels, and Combustion

The chemical, coal. H. H. LOWRY. *Ind. Eng. Chem.*, **26** [2], 133–39 (1934).—Not only as a source of energy but in all other fields of utilization, coal must undergo a series of chemical reactions to yield the end sought. The knowledge of the chemical nature of coal is based on the consideration of (1) its probable mode of origin, (2) its reactions with simple reagents, and (3) the products obtained by thermal decomposition. Correlation of the results obtained in the past two decades in investigations of coal by the three methods listed shows that considerable advance has already been achieved toward an understanding of the general chemical nature of coal. Solvent extraction, vacuum distillation, low-temperature carbonization, and high-temperature carbonization are discussed from the viewpoint of an increasing severity of thermal treatment. The progressive increase in molecular complexity and the persistence of the six-carbon ring from high-temperature tar to solvent extract are attributed directly to the structure of the original coal substance and are in accord with the data obtained in the study of the probable mode of formation of coal and in that of its reactions with chemical reagents. Since the conclusions reached are based on data for different coals and are derived from many sources, the relationships proposed may be inexact. Because of the complexity of the coal substance, the need for additional systematic work, using all available methods of attack, is emphasized. Illustrated. F.G.H.

Proposed simplification of the Parr unit coal formula. G. THIESSEN. *Fuel Sci. Practice*, **12** [12], 403–11 (1933). F.G.H.

Significance of solvent extraction and rational analysis in coal carbonization. E. B. KESTER, E. J. SCHNEIDER, AND F. W. JUNG. *Ind. Eng. Chem., Anal. Ed.*, **6** [2], 98–103 (1934).—From an intensive study of the relationship between solvent extraction or rational analysis data and other properties of coal, it is concluded that little may be interpreted from a knowledge of the quantities of extractable constituents present, with respect to significant differences in the restricted range of coking coals. F.G.H.

Technical utilization of natural gas. C. PADOVANI. *Acqua e Gas.*, **2**, 37–42 (1933); abstracted in *Bibliografia Italiana* [Series C], **6** [11–12], 41 (1933).—The use of natural gas for technical purposes is discussed, and consideration is given to various methods for converting it into a fuel with a lower heating value, thus making it comparable with artificial gas. H.F.V.

Use of alkaline pyrogallate solution in gas analysis. J. S. HALDANE AND R. H. MAKGILL. *Analyst*, **58** [7],

378 (1933); abstracted in *Fuel Sci. Practice*, **12** [8], 290 (1933). F.G.H.

Effect of hydrocarbons in gaseous fuels. W. BRASS. Sprechsaal, **66**, 45–46, 62–64 (1933); abstracted in *Fuel Sci. Practice*, **12** [12], 427 (1933).—The carbon particles produced in the course of the thermal decomposition of the hydrocarbons in gaseous fuels increase the amount of heat emitted due to their radiation. They also act as catalysts and thus accelerate the rate of combustion. Consequently the attainable temperature and the useful effect of gaseous fuels containing hydrocarbons are greater than those of gases not containing hydrocarbons with fuels of the same composition and thermal units. F.G.H.

Twenty-five years of natural and refinery gases. G. A. BURRELL. *Ind. Eng. Chem.*, **26** [2], 143–50 (1934).—The development in the natural gas industry is reviewed, including a discussion of the chemistry, transmission, purification, combustion, liquefaction, and by-products of natural gas. Illustrated. F.G.H.

Development of a formula to determine CO_2 in products of combustion. P. B. PLACE AND J. CRUISE. *Combustion*, **5** [10], 28 (1933); abstracted in *Fuel Sci. Practice*, **12** [11], 398 (1933). F.G.H.

Determination of the volume of the products of combustion. P. DI MAIO. *Calore*, **4**, 83–86 (1933); abstracted in *Bibliografia Italiana* [Series A], **6** [9–10], 27 (1933).—A formula for the rapid determination of the total volume of the products of combustion of 1 kg. of fuel as a function of the heating value of the fuel and the analysis of the flue gas is illustrated. H.F.V.

Ratio of hydrogen to carbon monoxide in products of combustion. JEROME J. MORGAN AND CHARLES STOLZENBACH. *Gas Age-Rec.*, **73** [13], 301–304 (1934).—Experimental evidence shows that when carbonaceous fuels containing sufficient hydrogen are burned under conditions such that the free hydrogen in the products of incomplete combustion does not exceed 3%, the ratio of the volume of carbon monoxide to the volume of hydrogen is a constant having a value of 2.9. A plausible explanation of this constant ratio is that the water-gas reaction controls the ratio between carbon monoxide and hydrogen in the combustion products. The value, 2.9, is also indicated as the ratio between the volumes of carbon monoxide and hydrogen in the analyses of the combustion gases from bituminous coal reported by Kreisinger, Augustine, and Ovitz of the U. S. Bureau of Mines. E.J.V.

Possibility of increasing the output of industrial furnaces by means of blasting secondary air. A. JAESCHKE. *Glashütte*, **63** [45], 740–42 (1934).—After discussing processes taking place during the firing of industrial gas furnaces working with secondary air, J. points out that the increase of the output of an industrial furnace (glass-melting furnace or muffle kiln) by means of supplementary blasting of secondary air has always been unsatisfactory. M.V.K.

Solving problems in firing. ANON. *Brick Clay Rec.*, **84** [3], 86–88 (1934).—A detailed description of how a problem in kiln firing was solved with the following results is given: (1) reduction in fuel cost, (2) reduction in firing time, (3) production of clean, clear colors, (4) elimination of seconds and culls, and (5) production of new colors. E.J.V.

Chamber drier utilizing air under pressure and initial humidity drying. P. THOR. *Ziegelwelt*, **64**, 151 (1933).—A drier is described which consists of nine or more chambers working in groups of three or more, the flues, etc., being so arranged that each group is fed with moist air, hot air, or waste-heat gases. The drier is the subject of a German patent. (*T.C.S.E.*)

BULLETIN

Investigation of the Accuracy of Routine Analytical Determinations on Coal and Coke. H. V. A. BRISCOE, J. H. JONES, AND C. B. MARSON. Fuel Research, Physical and Chemical Survey of the National Coal Resources, No. 29. H. M. Stationery Office, London, 1933. Price 10d. Reviewed in *Fuel Sci. Practice*, **12** [12], 430 (1933). F.G.H.

PATENTS

Method of operating fuel burning apparatus. R. C. BENNER, G. J. EASTER, AND B. W. STROMBERG (Carborundum Co.). U. S. 1,955,574, April 17, 1934. In the process of burning powdered coal, the steps which comprise introducing a reagent into the combustion chamber during the process of combustion for altering the melting point of the coal ash and varying the effective amount of reagent with variations in the flame temperature to maintain a substantially uniform temperature differential between the melting point of the coal ash and the flame temperature.

Muffle kiln. J. G. STEIN AND CO., LTD., J. F. HYSLOP, AND H. C. BIGGS. Brit. 406,459, March 7, 1934.

Means for supporting pottery ware during firing operations. C. E. R. TERRY. Brit. 406,809, March 14, 1934.

Geology

Nature of kaolin and clay in ceramics. K. ENDELL. Presented at the International Ceramic Congress, Milan, 1933; abstracted in *Tonind.-Ztg.*, **57** [101], 1198 (1933); *Sprechsaal*, **66** [52], 885 (1933).—Debye-Scherrer diagrams of fifty kaolins and clays from Germany, England, Bohemia, and U. S. prove the different structure of montmorillonite. The photometric determination of the dimensions of the interference lines permits the measurements of small fractions of clays in the region of $10\mu\mu$ to 1μ. The results of the X-ray determination of the structures of ceramic clays are discussed. It was found that by changing the individual complex coating of kaolin and bentonite, a far-reaching effect on plasticity, shrinkage on drying and crushing strength can be obtained. M.V.K.

Chemico-mineralogical composition of Kurinskii clays. A. FEDOSEEV. *Trans. State Ceram. Research Inst.* [Moscow], No. 35, pp. 14–33 (1932).—The chemical character-

istics of the clays vary. They contain from 40 to 66% SiO_2, 20 to 38% Al_2O_3, 1 to 12% Fe_2O_3, and up to 1% K_2O + Na_2O. The quantitative mineralogical analysis showed that the chief mineral components are kaolinite, muscovite, quartz, pyrite, and rutile. The clays are classified. M.V.K.

Fundamental properties of Ontario clay and shale. R. J. MONTGOMERY. *Can. Chem. Met.*, **18** [3], 53 (1934).—Lorraine shale, Queenston shale, sewer-pipe clay, upper interglacial clay, and lower interglacial clay samples were tested. The temperature of plastic flow, thermal expansion, and elasticity of these clays and shales suggests that the critical temperature interval for these bodies is from 500 to 600°C, and this range would merit additional investigation. E.J.V.

Italian raw materials for the glass and ceramic industries. ANTONIO ANFUSO. *Verre & Silicates Ind.*, **5** [3], 47 (1934).—Data on kaolin deposits found in Italy show that the deposits are homogeneous. The alumina content is not less than 40%; the total silica content amounts to 57%, of which 37% is combined with the alumina. The vitrification temperature reaches 1730°. The content of impurities is low. M.V.K.

Composition of pegmatitic feldspars as a criterion of their hydrogenetic origin. E. ZANIEWSKA-CHLIPALSKA. *Arch. minéral. soc. sci. Varsovie*, **7**, 49–81 (1931).—Klesów microcline has the composition SiO_2 64.55, Al_2O_3 18.90, Fe_2O_3 0.33, BaO 0.20, CaO 0.32, K_2O 13.13, Na_2O 2.17, H_2O 0.38%. Feldspars of igneous origin have the ratio $Al_2O_3 : SiO_2$ = 1:6; for those of pegmatitic origin it is 1:<6. This indicates the hydrogenetic origin of such feldspars as would have been deposited from colloidal solutions of igneous feldspar. (*C.A.*)

Chemical composition of pegmatitic and magmatic feldspars. K. CHUDOBA. *Centr. Mineral. Geol.*, **A**, pp. 260–73 (1933).—It has been stated by Thugutt (*Arch. minéral. soc. sci. Varsovie*, **1**, 59 (1926)) and by Zaniewska-Chlipalska (see preceding abstract) that feldspars of pegmatitic origin always deviate in chemical composition from the normal ratio, $R_2O:Al_2O_3:SiO_2$ = 1:1:6, and that such deviation may be a guide to the origin of a feldspar. Statistical consideration of a large number of analyses shows that magmatic and pegmatitic feldspars diverge in composition from the normal to an equal extent. The divergence may be due to microscopic inclusions of other minerals and gives no clue as to the genesis of the feldspar. Pegmatitic feldspars may perhaps be distinguished by their higher content of the rarer elements, but the evidence is inconclusive. (*C.A.*)

Differential thermal analysis of montmorillonite clays (bentonites). J. ORCEL AND S. CAILLÈRE. *Compt. rend.*, **197** [15], 774–77 (1933).—By applying the differential thermal analysis of Le Chatelier it has been possible to distinguish better than by other methods the similar forms of kaolinitic and montmorillonitic clays and to determine the sometimes small contents of kaolin by the temperatures where endothermic phenomena take place. M.H.

Boron derivatives in the glass industry. ANON. *Rev. Prod. Chim.* (Dec., 1933); abstracted in *Verre & Silicates Ind.*, **5** [4], 71 (1934).—By replacing a part of silica and soda by borax, glasses more resistant chemically and mechanically can be obtained. The duration of the fusion is shortened and the glass is more brilliant and has fewer defects. Borax and boric acid are also employed in the manufacture of special glasses of the Pyrex brand type for cooking, laboratory apparatus, etc.; borax is used in the production of crystal glass, and borax and boric acid, the latter especially, in ceramics and in the manufacture of porcelain because boric acid forms a vitreous coating on fusion when combining with the bases. The facility with which boric acid combines with metallic oxides permits varied decorative effects to be obtained. A borosilicate enamel has a greater covering power than lead enamels. Some products contain both lead and boric acid. M.V.K.

Boric acid. Its extraction in Tuscany. A. GRANGER. *Céram., Verrerie, Email.*, No. 6, pp. 293–95 (1933).—G. reviews and discusses developments in the extraction of boric acid in Tuscany. The acid, with several other salts, is found in geysers which have a temperature of about 205°C. This heat is used to evaporate the salts to dryness. M.H.B.

Anhydrous silicates of aluminum in south Australia. J. W. ILIFFE. *Sands, Clays, & Minerals*, **2** [1], 27–32 (1934).—Minerals of the formula $Al_2O_3.SiO_2$ without water in chemical combination are plentiful in the northeastern parts of south Australia and in New South Wales. Andalusite, sillimanite, fibrolite, and cyanite are described. They are excellent materials for the manufacture of refractories. M.H.

Actualities of the bauxite industry. V. CHARRIN. *Céram., Verrerie, Email.*, No. 5, pp. 249–50 (1933).—The bauxite industry in France has fallen off considerably due to the small size of high-grade bauxite deposits and the poor quality of the larger deposits. M.H.B.

Analysis of zircon sand. W. R. SCHOELLER. *Sands, Clays, & Minerals*, **2** [1], 7–10 (1934).—The chemical examination of zirconium minerals is described. They are easily identified under the microscope by their highly refractive tetragonal crystals consisting of a prism capped with a pyramid at either end. They may be brown, pine, red, or colorless. Triplicate portions of 0.5 g. each are used for chemical analysis. The procedure of separating titania, alumina, thoria and ceria, and phosphoric anhydride is given in detail. M.H.

Story of Canadian mining. I. FREDERICK EDWARDS. *Can. Mining Jour.*, **55** [3], 114–21 (1934).—The history of mineral exploration and development up to 1842 is given. G.M.H.

BOOK AND BULLETINS

Minerals and the Microscope. 3rd ed. H. G. SMITH. xiii + 124 pp., 12 plates, 33 figs. Thos. Murby and Son, London, 1933. Price 5s. Briefly reviewed in *Econ. Geol.*, **29** [1], 100 (1934).—The new edition differs in its treatment of rocks. It includes ideas developed in petrology since 1919, the date of the second edition. Emphasis is placed on differentiation and assimilation to account for variations in rock types. J.L.G.

Iron oxide mineral pigments of the United States. HEWITT WILSON. *Bur. Mines Bull.*, No. 370, 198 pp., 15¢ from Supt. of Documents, Washington, D. C. W. reviews the occurrence of mineral pigments and allied

iron ores and the nomenclature and common methods of classifying and testing many commercial pigments used in the U. S. R.A.H.

Mineral physics studies. R. S. DEAN, V. H. GOTTSCHALK, JOHN GROSS, J. KOSTER, C. W. DAVIS, AND C. E. WOOD. *Bur. Mines Rept. Invest.*, No. 3223, 37 pp. Free. The following papers make up this report: (1) magnetic separation of minerals; (2) deformation of solids; (3) progress in explosive shattering; (4) measurement of crushing resistance of minerals by the scleroscope; and (5) preliminary report on dust settling. R.A.H.

Chemistry and Physics

Phase diagram for ternary mixtures. V. FISCHER. *Ann. Physik*, **17**, 421–24 (1933).—A concentration-temperature diagram has been developed for ternary mixtures. Its use is shown for the mixture oxygen, nitrogen, and argon. Isobars are drawn for this mixture. W.M.C.

Equilibrium diagram of the iron-aluminum system. A. OSAWA. *Sci. Repts. Tôhoku Imp. Univ.*, **22** [4], 803–23 (1933).—The study of this diagram has been carried out by means of X-rays and microscopic examinations. Four compounds have been found: $(FeAl)_2$, $FeAl_2$, Fe_2Al_5, $FeAl_3$. The crystal structures of the alloys were determined using single crystals. The compound $FeAl_3$ solidifies from the melt directly. It shows a maximum melting point on the liquidus curve. A eutectic is formed with aluminum on one side and a second one with Fe_2Al_5 on the other side. W.M.C.

The periodic table. B. S. HOPKINS. *Jour. West. Soc. Engrs.*, **38** [6], 307–18 (1933).—H. discusses the periodic table and the part it has played in developing modern civilization. The date of discovery, the discoverer's name, and the general method of discovery are given for all elements for which this information is known. Atomic structure is explained and the various uses of the different elements are mentioned. Illustrated by charts. J.L.G.

Glassy phase of various ceramic materials. BERNARD LONG. Presented at the International Ceramic Congress, Milan, 1933; abstracted in *Sprechsaal*, **66** [52], 886 (1933); *Glashütte*, **63** [49], 835 (1933); *Tonind.-Ztg.*, **57** [101], 1198 (1933).—It is known that glass has a so-called transformation point; most of the dense ceramic materials also have a glassy phase and therefore show certain constitutional analogies with devitrified glasses. When examining their expansion before and after quenching, the existence of a glassy phase may be ascertained and the conditions of cooling after firing determined. The cooling of strongly vitrified ceramic bodies must follow the same principles as the cooling of glass. M.V.K.

Contribution to the question of plasticity. K. PFEFFERKORN. *Sprechsaal*, **67** [7], 93–94 (1934).—The chief reason of the plasticity phenomenon is the accumulation of water by the kaolinite (clay substance) molecule. Attempts to produce plastic masses from feldspar, sand, and a water-glass solution are described. A high plasticity was obtained with silicic anhydride containing water. See also *Ceram. Abs.*, **12** [7], 280 (1933). M.V.K.

Mechanics of plastic deformation: flow of Duralumin through orifices. S. I. GOUBKIN. *Jour. Rheology*, **3** [4], 501–48 (1932).—The theory of working materials under pressure is developed. The pressure of flow depends on kind of material, cast, annealed, etc., temperature of treatment, degree, rate, and type of deformation, geometrical form of material, and type of stressed condition. Although the physicochemical analysis was made on a metal, Duralumin, the theory is applicable to other viscous materials such as glass. Bibliography. M.H.

Potash and alumina from Georgia shale. S. L. MADORSKY. *Ind. Eng. Chem.*, **26** [3], 256–59 (1934).—In the chemical extraction of potash from shales, as typified by the extensive Georgia shales, containing 7 to 8% potassium oxide, the separation of alumina as a by-product enhances the economic potentialities of the operation. Studies are presented on the separation of alumina in pure form from the other constituents of the mineral rendered soluble by a hydrochloric acid extraction. Subjecting the mixed chlorides to a heat treatment in an atmosphere of hydrochloric acid gas converts the aluminum chloride to the oxide, the other constituents remaining as the water-soluble chlorides. Illustrated. F.G.H.

Analytical reactions of rubidium and caesium. W. J. O'LEARY AND J. PAPISH. *Ind. Eng. Chem., Anal. Ed.*, **6** [2], 107–11 (1934).—A critical résumé is given of the known analytical methods for determining potassium, rubidium, and caesium. A reaction of rubidium and caesium is described which affords a satisfactory separation of these elements from potassium. A modification of the standard chloroplatinate procedure is suggested, and an improved method is proposed for the quantitative separation and determination of potassium, rubidium, and caesium, based on the use in succession of 9-phosphomolybdic, silicotungstic, and chloroplatinic acids. F.G.H.

Study of synthetic cryolite analysis. F. J. FREERE. *Ind. Eng. Chem., Anal. Ed.*, **6** [2], 124–25 (1934).—F. points out the differences between natural and synthetic cryolite, identifies some of the chief components, and tests the applicability of certain procedures which may ultimately lead to an acceptable method of analysis. F.G.H.

Action of sodium amide on silicates and refractories. P. V. PETERSON AND F. W. BERGSTROM. *Ind. Eng. Chem., Anal. Ed.*, **6** [2], 136–38 (1934).—A large variety of silicon-containing substances, including feldspar, bauxite, serpentine, soapstone, soda-lime and Pyrex brand glasses, fired refractories, and clay, are completely decomposed by fused sodium amide. The aqueous solution of the fusion contains all of the silica as sodium silicate, and silicon may therefore be determined accurately by the usual methods of quantitative analysis. The specimens for analysis must be finely ground, preferably to 200-mesh per inch or finer. In the case of an easily fusible silicate, feldspar, the minimum fusion time, at

the end of which sensibly complete decomposition of the 200-mesh material has taken place, is about 30 min. at 330°C. It is recommended that the time of fusion of material of unknown behavior be 2 to 3 hr. at 330°C. Alundum is not completely broken down by fused sodium amide under optimum conditions in 9 hr., and it therefore can not be analyzed by this method without undue expenditure of time. The use of nickel crucibles for the fusion eliminates the more costly platinum crucibles necessary in fusions of silicate ores with sodium carbonate or hydroxide. F.G.H.

New volumetric method for determination of sulfate. V. R. Damerell and H. H. Strater. *Ind. Eng. Chem., Anal. Ed.*, **6** [1], 19–21 (1934). Standard barium chloride solution is added to the solution containing sulfate, using mercuric nitrate as an outside indicator. A technique is described in which a preliminary end point is reached several cubic centimeters in advance of the final end point, enabling the analyst to add the bulk of the barium chloride solution rapidly. F.G.H.

Determination of borate ion in ores of borax. H. L. Payne. *Ind. Eng. Chem., Anal. Ed.*, **6** [1], 45–46 (1934). F.G.H.

Detection and estimation of small amounts of fluorine. I. M. Kolthoff and M. E. Stansby. *Ind. Eng. Chem., Anal. Ed.*, **6** [2], 118–21 (1934). F.G.H.

Determination of silica in silicates by difference. G. T. Galfajan and W. M. Tarajan. *Z. anal. Chem.*, **92**, 417–20 (1933).—Criticism and modification of the method proposed by Tananaeff and Perchik (*Ceram. Abs.*, **11** [11], 595 (1932)) is presented. Oxalic acid is not suitable for converting the fluorides into carbonates and oxides. To 0.5 to 1.0 g. of finely powdered silicate moistened in a platinum crucible with 15 to 20 drops of sulfuric acid (1:1) 5 to 7 cc. of hydrofluoric acid are added and the mixture is evaporated on a steam bath. Excess H_2SO_4 is removed by careful heating on a sand bath, a few more drops of H_2SO_4 are added, and the mixture is again heated until white SO_3 fumes appear. After 3 to 4 g. of sodium metaphosphate have been added to the dry mixture it is ignited to constant weight. This method is suitable for silicates having low or high alumina contents. The degree of accuracy is high, and a determination can be carried out in 5 or 6 hr. E.J.V.

Determination of cobalt, nickel, and copper with anthranilic acid. H. Funk and M. Ditt. *Z. anal. Chem.*, **93** [7–8], 241–47 (1933).—Methods are described whereby cobalt, nickel, and copper can be determined quickly and with considerable accuracy. Due to the favorable conditions in weighing out the materials, which amount to 5 to 6 times the existing amount of the metal being determined, as well as the favorable reduction factor for the volumetric determination, proportionately small amounts can be determined with accuracy. The precipitates can be filtered easily, especially if care is taken to avoid a sudden suction during filtration by proper filling of the filter funnel. E.J.V.

Determination of beryllium. L. Fresenius and M. Frommes. *Z. anal. Chem.*, **93** [7–8], 275–79 (1933).—A review of methods of determining beryllium is presented. A series of experiments in which the beryllium is converted to the chloride and then ignited to beryllium oxide are described. There is no loss of beryllium due to the volatilization of the chloride if the hydroxide precipitate is ignited before it is washed free of ammonium chloride. It is shown that the beryllium chloride solution can be evaporated to dryness and ignited to chloride-free beryllium oxide without any loss. E.J.V.

Determination of the refractive indices of solids. A. Biot. *Rev. d'Optique*, **11**, 481–500 (1932). (*J.S.G.T.*)

Transport of matter in solid substances. G. v. Hevesy. *Z. Elektrochem.*, **39** [7*b*], 490–500 (1933).—In consequence of the weakening of interionic forces and the higher spatial ionic concentration the fusions of strong electrolytes show high conductivities. The transport of matter in fusions does not exhibit such specificity; the velocities with which Ag^+ and Cl^- ions, *e.g.*, move in fused AgCl differ only slightly. The transport of matter is believed to be an inherent property of energy-rich solid substances. The accumulation of energy in different places in a crystal permits lattice ions to leave their positions. Chemically different crystals are acted upon to a varying extent by this added energy according to the size, charge, and polarization properties of the lattice ions. Grain refinement and similar disorders of formation of ideal crystal structures are also produced thereby. E.J.V.

Determination and valuation of the melting point of ashes. Bretislav G. Simek, Frantisek Confalik, and Zdenek Beranek. *Feuerungstechnik*, **22** [1], 1–6 (1934).—The temperatures of the melting point of ashes were determined by means of two macroscopic methods, thermoelements and Seger cones. The methods yield good results provided the temperature is measured exactly. M.V.K.

Action of electrolytes on solutions of kaolin. Pichot. *Compt. rend.*, **197** [6], 451–53 (1933).—When stirring clay or kaolin in distilled water a disperse system of almost ultra-microscopic particles is obtained. The clarification of this cloudy solution can be influenced by the addition of electrolytes; if the clarification is accelerated the electrolyte is called flocculent, if it is influenced only slightly, peptisant. The opacity changes of the solution with time were investigated for different solutions of NaCl. M.H.

Thermal decomposition of magnesium silicides. G. Gire. *Compt. rend.*, **196** [19], 1404–1406 (1933).—The existence of a compound, SiMg, is confirmed which is stable only above 800°; at 600° it decomposes slowly according to $2SiMg \longrightarrow SiMg_2 + Si$. $SiMg_2$ is unstable above 600° and decomposes according to $SiMg_2 \longrightarrow SiMg + Mg$. Synthetically prepared $SiMg_2$ was not stable above 500° and gave another compound, Si_2Mg_3, in the decomposition which is also unstable. M.H.

Thermal expansion of zinc by the X-ray method. E. A. Owen and John Iball. *Phil. Mag.*, **16**, 479–88 (1933).—The thermal expansion of zinc has been found to depend upon the degree of regularity of the arrangement of the crystals, for the expansion depends upon the direction of measurement with respect to the axis, differing when parallel to a hexagonal axis and when perpendicular to the axis. The expansion coefficients parallel and perpendicular to the axes are measured by means of a displacement of the X-ray fringes. No high order of accuracy is claimed. Measurements are made up to 400°C, the value perpendicular to the hexagonal axis being (20 to

250°) 1.5×10^{-6}, (20 to 350°) 1.7×10^{-6}, (20 to 400°) 1.6×10^{-6}; the corresponding values parallel to the axis are 5.3×10^{-6}, 5.5×10^{-6}, and 5.9×10^{-6}, respectively. J.T.L.

Thermal investigation of lime-silicic acid phosphates. G. BEHRENDT AND H. WENTRUP. *Arch. Eisenhüttenwesen*, **7**, 95–102 (1933).—A new sensitive radiation thermocouple records small heat reactions. Synthetic mixtures of a composition similar to that of (basic) Thomas slag show the existence of silico-carnotite. The melting temperature of this compound is 1900°. A ternary eutectic exists between lime, silico-carnotite, and tetra-phosphate, the freezing temperature being between 1595 and 1600°. No second ternary eutectic was found. Sections vertical to the plane of concentration result in quasi-binary sections if laid through silico-carnotite and tetra-phosphate or through silico-carnotite and binary phosphate. W.M.C.

Diffusion of monatomic gases through fused silica. T. ALTY. *Phil. Mag.*, **15** [7], 1035–48 (1933).—The existing data in the literature on the rate of diffusion of gases through solids are reviewed and shown to be consistent with the theory that monatomic gases enter fused silica directly from the gas phase and the points of entrance are narrow cracks along the crystals. J.T.L.

Determination of the surface area of dense and porous bodies. H. KÖNIG. *Arch. Eisenhüttenwesen*, **7**, 441–44 (1933).—The surface area of a dense body may be calculated from its volume only after introducing a variable factor, α. Photographic means allow the shape of the surface to be determined exactly. No satisfactory method is known which might be used in determining the surface area of porous substances. It is proposed to polish a small part of the surface and to count the number of pores. Samples are given for both methods. W.M.C.

Compilation of specific heat data used for metallurgical calculations. C. SCHWARZ. *Arch. Eisenhüttenwesen*, **7**, 281–92 (1933).—Interpolation formulas are presented. Bibliography. W.M.C.

Bauxite as a flux in the basic open-hearth (steel) process. F. H. SCHÖNWÄLDER. *Stahl & Eisen*, **53** [37], 949–52 (1933).—Experiments were carried out replacing fluorite as a flux by bauxite. Advantages of bauxite over fluorite are claimed to be (1) its instantaneous action on the slag, decreasing its viscosity, (2) the greatly reduced destruction of the furnace lining, (3) economy, (4) smaller heat radiation of bauxite slag, and (5) earlier removal of gases. W.M.C.

Rational analysis of clay. A. GRANGER. *Céram., Verrerie, Email.*, No. 4, pp. 197–99; No. 5, pp. 245–47 (1933).—G. reviews some of the difficulties encountered in the rational analysis of clay. He points out that the results obtained vary widely with those of different investigators and may not be taken as conclusive. M.H.B.

Characteristic surface number of fine-grained materials as an expression of their degree of fineness. R. STUCHTEY. *Glückauf*, **70** [2], 41–43 (1934).—When classifying according to mesh, *i.e.*, grain size, the surface of each grain size in cm.²/g. is determined and the sum of all surfaces of the meshes determined is considered as characteristic for the fineness of a material. An example illustrates the method. M.H.

BOOK REVIEW

Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. Vol. XVIII. Published by the Society of Chemical Industry, London, 1933. 777 pp. Chapters of interest to ceramists are (1) general plant and machinery, (2) fuel, (3) glass, (4) refractories, ceramics, and cements, and (5) soils and fertilizers. These chapters are a summary of the advances made during the past year in each of the fields listed. Of particular interest to those who have been seeking an explanation of the behavior of slips in the exchangeable bases of clays is the chapter on soils and fertilizers. The sections on "minerals of soils and clays" and "ionic exchange and the structure of silicates" gives several references to original papers on this work. Considering the limitations of a publication of this kind the fields are well covered although some work of merit is overlooked. A.J.METZGER

BOOKS

Handbook of Chemistry and Physics. C. D. HODGMAN. 18th ed. Chemical Rubber Publishing Co., Cleveland, Ohio. 1818 pp. Price $6.00. Reviewed in *Foundry*, **62** [2], 48 (1934); *Ind. Eng. Chem., News Ed.*, **12** [1], 18 (1934); for 17th ed. see *Ceram. Abs.*, **12** [5], 207 (1933). F.G.H.

Chemical Engineers' Handbook. Edited by J. H. PERRY AND W. S. CALCOTT. 1st ed. McGraw-Hill Book Co., Inc., New York, 1934. 2609 pp. Price $9.00. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [5], 93 (1934). F.G.H.

PATENTS

Titanium phosphate pigment and process of making. B. D. SAKLATWALLA, H. E. DUNN, AND A. E. MARSHALL (Southern Mineral Products Corp.). U. S. 1,953,777, April 3, 1934.

Crystallization of sodium metasilicate hydrates. M. C. WADDELL (Grasselli Chemical Co.). U. S. 1,953,839, April 3, 1934.

Process for making sodium pyrosilicate hydrate. M. C. WADDELL (Grasselli Chemical Co.). U. S. 1,953,840. April 3, 1934.

Silicates. C. L. BAKER (Philadelphia Quartz Co. of California, Ltd.). Fr. 725,923, June 30, 1931. Stable crystal hydrates of alkali metal silicates are prepared from solutions of alkali metal silicates by regulating the solutions at high temperatures according to the amount of water necessary to obtain the desired hydrate and bringing the solutions to crystallization at temperatures corresponding to or slightly below the melting point of the desired hydrate. Fr. 41,736, March 29, 1933; addition to Fr. 725,923. Crystalline hydrates of alkali silicates, *e.g.*, hydrates of Na metasilicate, are prepared from solutions of alkali silicates in which the molecular ratio of SiO_2 to alkali oxide corresponds to that of the crystals to be made, the amount of water being regulated at a high temperature, approximate to that required for the hydrate. The solutions are brought to partial crystallization at a temperature slightly below the freezing point of the hydrate desired, with very gradual admission of heat and energetic agitation, during a prolonged period. The mother liquor is afterward eliminated, *e.g.*, by centrifugation, from crystallized paste formed and the crystals are dried. (*C.A.*)

General

Ceramic Education. IV. Ross C. Purdy. *Bull. Amer. Ceram. Soc.*, **13** [4], 81–82 (1934).

Birth of the American Ceramic Society. H. A. Wheeler. *Bull. Amer. Ceram. Soc.*, **13** [4], 82–84 (1934).

Looking ahead. Editorial. *Bull. Amer. Ceram. Soc.*, **13** [4], 84 (1934).

Natural and artificial ceramic products. Arthur L. Day. *Bull. Amer. Ceram. Soc.*, **13** [4], 85–95 (1934). Illustrated.

An ancient art becomes a modern industry. Robert A. Weaver. *Bull. Amer. Ceram. Soc.*, **13** [4], 95–101 (1934). Illustrated.

Asheville Meeting program in detail. Anon. *Bull. Amer. Ceram. Soc.*, **13** [4], 102–104 (1934).

Spruce Pine mining center to be visited. B. C. Burgess. *Bull. Amer. Ceram. Soc.*, **13** [4], 104–105 (1934). Illustrated.

Minutes of combined meeting of Committee on Publications and Division Editorial Committees. Louis Navias and R. E. Birch. *Bull. Amer. Ceram. Soc.*, **13** [4], 107–108 (1934).

Refractories Division annual meeting minutes. Robert B. Sosman. *Bull. Amer. Ceram. Soc.*, **13** [4], 108 (1934).

Progress report of the Committee on Data. T. W. Garve. *Bull. Amer. Ceram. Soc.*, **13** [4], 108 (1934).

Annual report of Committee on Sections and Divisions. Emerson P. Poste. *Bull. Amer. Ceram. Soc.*, **13** [4], 109–10 (1934).

Necrology: David Raymond Edgar. Anon. *Bull. Amer. Ceram. Soc.*, **13** [4], 113 (1934).

Relationship between ceramic investigations and industry. G. Gianoli. Presented at the International Ceramic Congress, Milan, 1933; abstracted in *Tonind.-Ztg.*, **57** [101], 1197 (1933); *Sprechsaal*, **66** [52], 885 (1933); *Glashütte*, **63** [44], 724 (1933).—Questions, solutions of which are of great importance for technical progress, are discussed. They include (1) a method for increasing plasticity of kaolin and clay and their stability in the plastic state, (2) development of mineralizers promoting the tridymitization of quartz at lower temperatures, (3) development of protecting mixes for silicon carbide against corrosion by alkaline vapors in order to use it for saggers, (4) increasing the life of filter cloths, and (5) increasing the efficiency of furnaces. M.V.K.

Bases and aims of the science of construction. C. L. Ricci. *Ann. della R. Scuola d'Ing. di Napoli*, pp. 21–58 (1933); abstracted in *Bibliografia Italiana* [Series C], **6** [11–12], 105 (1933).—R. describes various branches of modern engineering, with special reference to the science of construction. H.F.V.

Testing of materials in ceramics. A. Hecht. *Keram. Rund.*, **42** [6], 71–73; [7], 83–87 (1934); abstracted in *Sprechsaal*, **66** [52], 885 (1933); *Tonind.-Ztg.*, **57** [101], 1196–97 (1933); *Glashütte*, **63** [49], 835 (1933).—The testing of materials in ceramics can be classified as (1) testing of raw materials, especially clay, (2) general determination of the properties of ceramic materials, and (3) special tests of finished products. When testing raw materials, the chemical and mineralogical composition, the presence of coarse and injurious ingredients, behavior on firing, firing color, and melting behavior are determined. The elutriation and sedimentation analyses, methods for ascertaining the softening of clays and mixes, and colloido-chemical methods for studying liquefaction and plasticity are discussed in detail. Other tests include determination of the structure by finding the specific gravity, volume weight, and capability of absorbing water and other liquids by means of gas-permeability and optical methods. The main strength tests are resistance to pressure, tensile strength, transverse strength, and resistance to torsion. The bending and torsion tests show elasticity (the determination of the behavior of refractories under load at high temperature also belongs to the strength test). Special thermal properties are the permanent and reversible changes in length on firing, thermal conductivity, and temperature stability. Other tests determine the resistance to attacking materials such as liquids, gases, and slagging materials as well as to mechanical wear. The determination of water tightness and air permeability, density, and freezing tests are important for brick and tile. For paving brick there are special impact strength tests, wearing tests, etc. Pipes are tested for bending and inner pressure. Tests for determining the harmfulness and cooking stability of cooking utensils and glazed ware have been developed. For fine ceramic ware the determination of stresses between the body and glaze, the impact strength tests, and measuring the hardness, luster, and color of glazes are important. The exact measurement of density and the determination of insulating resistance or impact strength for porcelain and other dense ceramic products have been especially well developed. M.V.K.

Value of silicate of soda as a detergent. III. Siliceous silicate in water containing either calcium bicarbonate or carbon dioxide. J. D. Carter and W. Stericker. *Ind. Eng. Chem.*, **26** [3], 277–81 (1934). F.G.H.

Detergents for metal cleaning. M. B. Peterson. *Metal Cleaning & Finishing*, **6** [3], 127–30 (1934).—In general, oxides or similar metallic compounds which constitute rust, scale, and tarnish and grease, oil, and other organic substances are the foreign materials which adhere to metal surfaces. Both the physical and chemical properties of a detergent are involved in removing these materials from metal. Among the detergents for metal cleaning are neutral and built soaps, alkalis, and hymolal salts. Each of the first three types has important uses in the metal cleaning field. Hymolal salts, salts of alcohols of high molecular weight, are the latest development in the detergent field. The new and distinctly different properties of hymolal salts are enumerated. Applications and functions of detergents are listed, and the possibility of applying hymolal salts to metal cleaning problems is discussed. E.J.V.

Gas correction factor. R. H. Parrish. *Factory Management & Maintenance*, **92** [2], 77 (1934).—The correction factor or multiplier commonly used in computing the monthly gas bills of industrial plants is explained. P. indicates how it is derived and how it may be checked. Its use is necessary whenever gas is supplied to a meter at a pressure higher or lower than the meter was built to mea-

sure. This is so because the meter will indicate the same volume of gas flowing whether it be at a pressure of 8 oz. or 2 lb. per sq. in., although a cubic foot at 2 lb. will obviously contain more heat units than a cubic foot at 8 oz. per sq. in. Since the number of heat units in a unit volume of gas is directly proportional to the absolute pressure at the meter, the correction factor can be expressed in terms of the ratio of absolute pressures if the temperature is assumed to be constant. The correction factor then becomes

$$\frac{\text{gage pressure} + (0.49 \times \text{barometer reading})}{\frac{\text{standard pressure (oz.)}}{16} + (0.49 \times \text{barometer reading})}$$

Since the temperature of the gas at the meter is usually more or less constant and since the computation of changes due to changes in seasonal temperature would entail a tremendous amount of extra labor in figuring monthly gas bills, it is usually neglected. It is evident, however, that the formula may readily be amended to correct for temperature using absolute temperatures in numerator and denominator but inversely placed with respect to standard and gage pressures. J.L.G.

Silicosis legislation. BENJAMIN F. TILLSON. *Eng. Mining Jour.*, **135** [2], 68–70 (1934).—Silicosis legislation is considered with special attention to proposals in N. J. T. lists 22 industries subject to dust hazards among which are found the majority of the ceramic industries. Although 44 states and 4 territories of the U. S. possess workmen's compensation laws not one specifically mentions silicosis or pneumoconioses (dust injuries to lungs). T. advocates silicosis compensation laws not only for the protection of the worker but also to safeguard the employer since at present there is little to guide compensation awards. The N. J. bill is being drawn by a committee of ten members, four lawyers, three doctors, a college professor of ceramics, an industrialist, and a member of organized labor. T. finds the bill too narrow in its application since it does not sufficiently cover the dangerous dusts and since the only injury to the lungs it considers is a substitution of fibrous tissue for the elastic tissue of the lung. A three-member permanent board of control is provided to consist of one medical man, one engineer, and one chemist. Dusts covered are listed as inorganic. This could be changed to a broader term to include coal, cotton, and hair dusts. Compensation liability is placed on the last employer although injuries from dusts are cumulative. Disability must have commenced within two years after the employee was last exposed to the dust. The employee's exposure to the dust must have continued for at least two years. T. states that several cases of silicosis are recorded where the exposure period varied from four to eighteen months. Hence the two-year period of exposure clause seems to specify too long a period. J.L.G.

Mortality experience of group exposed to silica dust compared with that of general population and group exposed to dust not containing silica. EDGAR L. COLLIS AND G. YULE. *Jour. Ind. Hygiene*, **15** [6], 395–417 (1933); *Amer. Jour. Pub. Health*, **24** [4], 405 (1934).—Statistics comparing the mortality experience of an occupational group exposed to silica with the two other groups are given. By standardizing the deaths it was found that the comparative mortality figures for all causes and all ages (20 to 65) were 1000 for the general population, 1984 for the silica group, and 967 for the nonsilica group. Comparison showed only three causes of the 23 cause groups studied (diabetes, appendicitis, and other diseases of the digestive tract) in which mortality of the silica group did not differ significantly from that of the standard population. Very high mortality (over double that of the standard population) resulted from pulmonary tuberculosis, other tuberculosis, chronic rheumatism, bronchitis, chronic interstitial pneumonia, other diseases of the respiratory system, and hernia. In the nonsilica occupational group mortality for influenza, pulmonary tuberculosis, bronchitis, chronic interstitial pneumonia, and other diseases of the respiratory system was higher than that of the general population. E.J.V.

Choosing the right drive. I–VI. WILLIAM STANIAR. *Iron Age*, **132** [3], 12–18; [7], 10–13; [12], 8–12; [16], 18–22; [20], 22–25; [25], 14–17 (1933); see *Ceram. Abs.*, **11** [1], 48 (1932). A.K.

BOOK REVIEWS

Pocketbook for Ceramists, 1934 (Taschenbuch für Keramiker, 1934). (In German only.) **Vol. I. A notebook-calendar.** 19 pp. **Vol. II. Technical section.** 368 pp. Published by Keramische Rundschau, Berlin. Price 3.30 Rm. The book deals with (1) structure of glasses, (2) their general properties, (3) safety glass, (4) raw materials and testing, (5) rational analysis, (6) testing methods for finished products, (7) structure of glazes and enamels, (8) index of German literature dealing with ceramics, (9) tables of general information, (10) list of supply firms, (11) patents, etc. M. V. KONDOIDY

Clay Industry Calendar, 1934 (Tonindustrie Kalender, 1934). (In German only.) 2 vols. Published by Tonind.-Ztg., Berlin. Price 3.30 Rm. Volume I is a notebook calendar and contains 19 pp. of tables and general information. Volume II deals with (1) the manufacturing processes of porous brick and nonporous hollow brick, (2) use of hollow brick, (3) mortar and masonry, (4) general information, (5) list of supply firms, (6) index of literature, and (7) patents, etc. M. V. KONDOIDY

BOOK AND BULLETIN

Cost and Production Handbook. Edited by L. P. ALFORD. Ronald Press Co., New York, 1934. 1544 pp. Price $7.50. Reviewed in *Ind. Eng. Chem., News Ed.*, **12** [3], 52 (1934).—An excellent section on development and research is included in this handbook of cost accounting for the industrial field. F.G.H.

PATENTS

Synthetic precious stone. MAX JAEGER AND HERMANN ESPIG (I. G. Farbenindustrie A.-G.). U. S. 1,952,255 and 1,952,256, March 27, 1934.

Roofing granules and method of producing. E. H. NICHOLS. U. S. 1,954,778, April 10, 1934. Roofing granules, each granule of which has a surface coating composed of partly fused granule particles and completely fused granule particles.

37th ANNUAL MEETING

OF THE

AMERICAN CERAMIC SOCIETY

HOTEL STATLER, BUFFALO, N. Y.

WEEK OF FEBRUARY 17, 1935

AND ANNUAL MEETING OF THE

NATIONAL BRICK MANUFACTURERS RESEARCH FOUNDATION

√ With the help of each member this Annual Meeting will continue the series of programs rich in information and of increasing value to the ceramic industries.

TECHNICAL MEETING PROGRAM COMMITTEE

Ex-officio Chairman
Ross C. Purdy,
General Secretary

Art
Arthur Baggs
H. S. Nash

Enamel
R. R. Danielson

Glass
U. E. Bowes

Materials and Equipment
G. H. Brown

Refractories
H. M. Kraner
K. E. Buck

Structural Clay Products
W. H. Vaughan

Terra Cotta
H. D. Callahan
W. L. Howat

White Wares
F. P. Hall
C. W. Parmelee